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ON THE REICH METHOD OF DETERMINING ARSENIC.

BY LEROY W. MCCAY.

In the year 1864 there was introduced by Reich into the assay laboratory of the Royal Smelting Works at Freiberg, Saxony, a method for determining arsenic in ores and metallurgical products, based upon the fact that arseniate of silver is insoluble in water. The method, subsequently modified by Richter, has been in exclusive use at the laboratory of the Works ever since the period of its introduction. This fact speaks for its success.

The following short description of the process is taken from Post's *Chemische Technische Analyse:*

About 0.5 gram of the finely pulverised substance is digested in a porcelain crucible, covered with a watch-glass, with concentrated nitric acid and under the influence of heat, until the residue assumes a lighter color and the sulphur which separates out has become of a pure yellow hue. After decomposition the glass is rinsed with a few drops of water, and the uncovered crucible heated upon the sand-bath in order to get rid of excess of acid. A complete evaporation is to be avoided. Four grams of sodium carbonate are now added, the mass is completely dried upon the sand-bath, four grams of potassium nitrate are introduced into the crucible, and the same is heated until its contents flow quietly. The melted mass is permitted to remain in this state for ten

minutes. After the crucible is cool it is brought into a dish, the fused mass is extracted with hot water, and the resulting solution filtered. The alkaline liquid which contains the arsenic as arseniate of sodium is acidified with a small quantity of nitric acid, placed for two hours upon a hot sand-bath, in order to get rid of the carbon dioxide, mixed with a sufficient amount of silver solution, and then carefully neutralised with dilute ammonia. Reddish-brown arseniate of silver is precipitated. The precipitate is filtered off, washed, well dried, shaken from the filter upon glazed paper, and the folded filter paper brought into a scorifier and ashed in a glowing muffle. When the scorifier is cold the precipitate is added to the remains of the filter, the scorifier charged with ten assay tons of lead, and the combined silver estimated in the ordinary way. From the silver found the arsenic present is calculated: 100 Ag = 23.15 As.

In 1883 I published an article upon a modification of this method, which will be found in the *Chemical News*, Vol. 48, No. 1232, p. 7. A few weeks before the appearance of my article I noticed in *Science*, Vol. 1, No. 15, a short account of Reich's method by Mr. Pearce, of the Colorado Smelting Works at Argo, Col. A detailed description by Mr. Frost of this modification of the process was published in the *Engineering and Mining Journal*, Vol. 35, p. 256, and subsequently copied into the *Chemical News*, Vol. 48, No. 1239, p. 85.

My modification of the Reich method differs from that of Mr. Pearce in that it is essentially a method of *rest*. In fact, while working up the process, I followed very closely the mode of procedure recommended by Drs. Kratschmer and Sztancovánszky in their volumetric method for determining phosphorus.[1] Mr. Pearce's modification consists in dissolving the arseniate of silver in nitric acid and titrating the silver with thiocyanate of ammonium according to Volhard.

During the last two years I have had ample opportunity for thoroughly testing this silver method for estimating arsenic. In conjunction with several of my pupils, among whom I am especially indebted to Mr. J. W. Phillips, the process has been subjected to an exhaustive examination, and since numerous improvements have grown out of our work, it seemed desirable to again write a

[1] Zeits. für analy. Chem. 21, 593.

description of the entire matter, directing attention to many little details which were omitted in the first paper, to the most accurate practical way of conducting the analysis of ores and metallurgical products, and, above all things, to a gravimetric modification which renders it possible to get results more accurate perhaps than those obtained by Mr. Pearce's volumetric process.

Nitrate of silver throws down from solutions of di- and tri-metallic alkali arseniates a highly characteristic reddish-brown precipitate of arseniate of silver which is readily soluble in ammonia and acids, but insoluble in water. If the solution contained a tri-metallic arseniate the fluid in which the precipitate is suspended exhibits a neutral reaction, whilst the reaction is acid if the solution contained a di-metallic arseniate. The acid reaction in this latter case arises from the fact that the nitric radical receives, for the three atoms of silver which it surrenders to the arsenic acid, only two atoms of alkali metal and one atom of hydrogen:

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

By a suitable neutralisation of this molecule of free acid the filtrate from the precipitate can be shown to contain no arsenic.

Since this subject of neutralisation is of immense importance, and since there seems to exist in the minds of some chemists a doubt respecting the possibility of obtaining a neutralisation so complete as to occasion a separation of all the arsenic and yet avoid the precipitation of oxide of silver, in the minds of others a suspicion that the arseniate of silver is not absolutely insoluble in the nitrate of ammonium formed, I think it were well to begin by discussing the relations which hold between arseniate of silver and the hydrate and nitrate of ammonium. I can accomplish my purpose best by directing attention to the following experiments:

Experiment 1.—1 cc. of an ordinary solution of nitrate of silver was brought into a small beaker, diluted to 25 cc., and heated to boiling. It was then rendered faintly but distinctly alkaline with ammonia. No precipitate settled as long as the liquid was hot. Upon cooling a faint opalescence made its appearance, and, after standing over-night, the liquid had deposited a very small precipitate of oxide of silver—a quantity, however, too minute to filter and examine.

Experiment 2.—2 cc. of the solution of nitrate of silver were brought into a beaker, diluted to 50 cc., and a few small crystals

of ammonium nitrate added. The liquid was then heated to boiling, removed from the flame, and rendered faintly but distinctly alkaline with ammonia. No precipitate of oxide of silver appeared; none had made its appearance at the end of an hour, after the expiration of which time the liquid had cooled to the temperature of the laboratory; nor could I, even after allowing the solution to stand forty-eight hours, detect the smallest precipitate of oxide of silver. (1) 10 cc. of this solution gave, with one drop of a solution of arsenic acid = 0.00025 gram arsenic, an immediate and decided precipitate of arseniate of silver. (2) 10 cc. of the solution gave, with one drop of a solution of arsenic acid = 0.0001 gram arsenic, an immediate and distinct precipitate of arseniate of silver. (3) 10 cc. of the solution gave, with one drop of a solution of arsenic acid = 0.00005 gram arsenic, an extremely faint but, nevertheless, instantaneous cloudiness, which, upon permitting the liquid to stand, separated as a tiny red precipitate.

Again, the following experiments:

Experiment 1.—5 cc. of a solution containing about 14.45 grams H_2KAsO_4 per litre were brought into a small beaker, 100 cc. water added, and the contents of the beaker heated to boiling. A sufficient quantity of nitrate of silver to combine with the arsenic was then added, the beaker was removed from the flame, and its contents were rendered faintly but distinctly alkaline with dilute ammonia. After stirring briskly and prolongedly, so as to coagulate the arseniate of silver and cause it to settle rapidly and completely, the beaker was put aside until its contents were cool. The liquid was then filtered and the precipitate washed by decantation until the washings gave no reaction for silver. The precipitate in the beaker was covered with 100 cc. water and allowed to stand twelve hours. 25 cc. were next filtered into a Nessler cylinder and tested for silver with hydrochloric acid, but with a negative result. The original filtrate from the arseniate of silver was treated with hydrochloric acid, the chloride of silver filtered off, and the filtrate from the same saturated with sulphuretted hydrogen. In three days no sulphide of arsenic had separated. The flask containing the filtrate was kept in the dark and well corked.

Experiment 2.—The above experiment was repeated with 10 cc. H_2KAsO_4 solution, but the results were identical with those obtained with 5 cc.

Experiment 3.—The experiment was tried a third time, and with 20 cc. H_2KAsO_4 solution. The results were the same as in both previous cases.

These five experiments go to show:

a. That a solution of nitrate of silver containing small quantities of nitrate of ammonium can be made faintly but distinctly alkaline and yet no oxide of silver will separate out.

b. That when a solution of an alkali arseniate, after the addition of nitrate of silver, has been rendered neutral or faintly alkaline to delicate litmus paper, the precipitation of the arsenic as arseniate of silver is complete.

c. That arseniate of silver is to all intents and purposes insoluble in water containing *small* quantities of nitrate of ammonium.

Why, when the reaction of the liquid in which the arseniate of silver is suspended proves faintly but distinctly alkaline, there should be no perceptible action of the ammonia on the reddish-brown precipitate I am unable to say with certainty. I think, however, that the explanation is this: There is really *no* free ammonia present. The alkaline reaction of the liquid is due to the oxide of silver formed by the action of the ammonia on the excess of nitrate of silver and kept in solution by the small amount of ammonium nitrate present.[1] A solution of oxide of silver in ammonium nitrate gives a strong alkaline reaction.

The Reich method for estimating arsenic admits of four modifications:

1. *Reich Method Proper.*—The Ag_3AsO_4 is cupelled in a muffle with lead and the resulting silver button weighed.

2. *Pearce's Modification.*—The Ag_3AsO_4 is dissolved in nitric acid and the silver determined by Volhard's method.

3. *Author's First Modification.*—The excess of a standard solution of silver is determined by Volhard's method. By subtraction the combined silver is found, and, by calculation, the arsenic.

4. *Author's Second Modification.*—The Ag_3AsO_4 is dissolved in a few drops of dilute ammonia and the resulting solution caught, evaporated, dried, and weighed in a little, thin platinum dish. From the total weight of the Ag_3AsO_4 the arsenic is calculated.

The last method of determining the arsenic is direct, while all the others are indirect. All four methods give results of an extraordinary degree of correctness, but modifications 2 and 4 are

[1] See Mr. Low's art. in Chem. News **48**, 85.

by far the simplest, most convenient and accurate. I shall confine myself to a discussion of these two.

Solutions for Analysis.—1. 4.95 grams pure, dry arsenious oxide were oxidised with fuming nitric acid, evaporated with sulphuric acid, neutralised with ammonia and diluted to a litre. 2. 25 grams of H_2KAsO_4 were dissolved in water and diluted to two litres.

Solutions for Volumetric Work.—1. $\frac{1}{20}$ normal solution of thiocyanate of potassium.[1] 2. A saturated solution of ferric ammonium sulphate. 3. Dilute ammonia—say one of strong ammonia to ten of water.

The estimations which I here offer as a proof of the accuracy of both modifications were made as follows:

The solution was brought into a beaker, 50 cc. of water were added, the liquid was rendered slightly alkaline with ammonia, and the whole heated to boiling. More than a sufficient quantity of nitrate of silver to combine with the arsenic was then run in, the beaker was removed from the flame and its contents were rendered faintly alkaline. This last operation was accomplished by bringing the beaker under a clip burette containing the dilute ammonia, and permitting the same to drop in slowly, the contents of the glass being kept in a constant and violent state of agitation. By means of this vigorous stirring the arseniate of silver is made to coagulate and settle completely, leaving the supernatant liquid clear. As soon as a drop of the ammonia no longer produced a cloud in the clear upper stratum of liquid, and the reaction of the same was just alkaline to delicate litmus, the contents of the beaker were again well stirred and the whole was permitted to stand until cold. This cooling was generally hastened by placing the beaker in a dish of cold water. The liquid was thereupon filtered, the reddish-brown precipitate washed by decantation and (1) dissolved in pure nitric acid, ferric sulphate added, and the silver determined with $\frac{1}{20}$ normal thiocyanate of potassium according to Volhard, or (2) dissolved in a little warm ammonia, caught, evaporated, dried, and weighed in a little, thin platinum dish.

$$324Ag = 75As = 99As_2O_3 = 115As_2O_5,$$
$$463Ag_3AsO_4 = 75As = 99As_2O_3 = 115As_2O_5.$$

That the gravimetric is theoretically more accurate than the volumetric modification will be evident at a glance.

[1] Modern system. See Clemens Winkler's little work, Die Maassanalyse nach neuem titrimetrischem System.

Determinations with First-Test Solution.

Volumetrically (Pearce).

No.	Cc. Solution.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	5	7.45	.0186	.0245	.0285
2	5	7.4	.0185	.0244	.0283
3	5	7.4	.0185	.0244	.0283

Again:

No.	Cc. Solution.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	10	15.05	.0376	.0496	.0577
2	10	15.05	.0376	.0496	.0577

Finally:

20 cc. solution = 30.1 cc. $\frac{N}{20}$KCNS = .0752 gram As = .0992 gram As_2O_3 = .1154 As_2O_5.

Gravimetrically (McCay).

No.	Cc. Solution.	Ag_3AsO_4.	As.	As_2O_3.	As_2O_5.
1	5	.1150	.0186	.0245	.0285
2	5	.1140	.0185	.0244	.0284
3	5	.1135	.0184	.0243	.0283

Again:

No.	Cc. Solution.	Ag_3AsO_4.	As.	As_2O_3.	As_2O_5.
1	10	.2318	.0375	.0495	.0576
2	10	.2315	.0374	.0494	.0575

Finally:

20 cc. solution = .4625 gram Ag_3AsO_4 = .0749 gram As = .0989 gram As_2O_3 = .1149 gram As_2O_5.

The arseniate of silver obtained in each of the above determinations was, after weighing, dissolved in pure nitric acid and the silver estimated with thiocyanate of potassium.

No.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	7.50	.0188	.0247	.0287
2	7.40	.0185	.0244	.0283
3	7.50	.0188	.0247	.0287

Again:

No.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	15.1	.0377	.0497	.0578
2	15.0	.0375	.0495	.0576

Finally:

.4625 gram Ag_3AsO_4 = 30 cc. $\frac{N}{20}$KCNS = .0750 gram As = .0990 gram As_2O_3 = .1150 gram As_2O_5.

Theoretically: 5 cc. test solution = .01875 gram As = .02475 gram As_2O_3 = .02875 gram As_2O_5.

10 cc. test solution = .03750 gram As = .04950 gram As_2O_3 = .0575 gram As_2O_5.

20 cc. test solution = .07500 gram As = .09900 gram As_2O_3 = .1150 gram As_2O_5.

It will at once be seen that the results obtained above agree in a very gratifying manner with those required by theory.

Determinations with Second-Test Solution.

Volumetrically (Pearce).

No.	Cc. Solution.	Cc. $\frac{N}{20}$ KCNS.	As.	As_2O_3.	As_2O_5.
1	10	20.70	.0517	.0683	.0793
2	10	20.65	.0516	.0681	.0791
3	10	20.65	.0516	.0681	.0791
4	10	20.75	0.518	.0685	.0795
5	10	20.75	.0518	.0685	.0795
6	10	20.70	.0517	.0683	.0793
7	10	20.70	.0517	.0683	.0793
8	10	20.75	.0518	.0685	.0795
9	10	20.70	.0517	.0683	.0793
10	10	20.65	.0516	.0681	.0791
11	10	20.70	.0517	.0683	.0793
12	10	20.70	.0517	.0683	.0793

Theoretically: 10 cc. = 0.0521 gram As.

By Holthof's Iodine Method 10 cc. = 0.0513 gram As.

Again:

No.	Cc. Solution.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	20	41.4	.1034	.1366	.1586
2	20	41.45	.1036	.1370	.1690
3	20	41.5	.1036	.1370	.1590
4	20	41.5	.1036	.1370	.1590

.1036 ÷ 2 = .0518 gram. Required, .0513 gram.

It sometimes happens that the solution to be tested for arsenic

contains small quantities of chlorine.[1] In this case chloride of silver will be precipitated along with the arseniate of silver, and since chloride of silver is soluble in ammonia, it is plain that an error will be introduced into the gravimetric modification. In order to steer clear of this difficulty and yet preserve the simplicity of the process, I endeavored to make nitric acid take the place of the dilute ammonia. In the former reagent arseniate of silver is readily soluble, while the chloride of silver remains upon the filter paper intact. However, upon simply evaporating the solution to dryness several times with small quantities of water, it is no easy matter to obtain a correct weight. It is invariably too high. The acid sticks to the residue most persistently. In one instance ten evaporations with small amounts of water failed to remove it all. If, however, after evaporation, the acid remaining be neutralised by moistening the residue with a few drops of dilute ammonia, it is only necessary to dry the contents of the dish on the water-bath and gently ignite in order to obtain a perfectly pure arseniate of silver.

Example.—10 cc. of first-test solution were precipitated with nitrate of silver, the precipitate was washed by decantation, filtered, and dissolved off the filter paper into a little platinum dish with a few drops of dilute nitric acid. The solution was evaporated on the water-bath, the residue moistened with dilute ammonia, dried, and gently ignited by playing the flame of a burner around the dish until the nitrate of ammonium had been volatilised. I obtained 0.2315 gram Ag_3AsO_4 = 0.0495 gram As_2O_3—the figures required by theory. The arseniate was dissolved in nitric acid and the solution, diluted to about 150 cc., titrated with thiocyanate. I used 15.05 cc. $\frac{N}{20}$ KCNS = .1625 gram Ag = .0496 gram As_2O_3.

The presence of chlorine, therefore, cannot be urged as an argument against the general use of the gravimetric modification.

The Reich method is admirably adapted for estimating arsenic in ores and metallurgical products. The method of procedure is this: The ore, speiss, matte or slag is ground to an impalpable powder and a convenient quantity weighed out in an ordinary, medium-sized platinum crucible. The crucible is then covered with a watch-glass having a hole drilled through its centre, and through this hole there are introduced into the crucible 5 cc. of

[1] This is especially so in the analysis of ores and metallurgical products. The alkalies used for fusing almost always contain some chlorine.

dilute nitric acid. Care should be taken that the nitric acid be properly diluted, otherwise a violent reaction may ensue and some of the material be thrown out of the crucible. Heat is applied, and as soon as reaction sets in the crucible is put in a cool place and permitted to stand until the evolution of orange fumes ceases. The glass is rinsed with a few drops of water which are allowed to drain into the crucible and the solution is evaporated on the water-bath to the consistency of paste. Five to six times the weight of a mixture of four parts sodium carbonate and one part sodium nitrate are brought into the crucible and the whole is well mixed with a stout platinum wire. The substance adhering to the wire is thoroughly dried, and then, by means of a bit of broken glass, scraped back into the crucible. A little sodium carbonate is now sprinkled over the mixture, the lid of the crucible put on, and the whole gently heated by playing the flame of a burner around the crucible until all moisture is expelled. The contents of the crucible are gradually heated to fusion and kept in this state for about fifteen minutes. The fused mass is extracted with hot water, the oxides of the heavy metals are filtered off, and the filtrate is rendered weakly acid with nitric acid.[1] It is then boiled to expel carbon dioxide and evaporated to dryness. The residue is heated, taken up with water, and the solution filtered into a measuring flask. The flask is filled to the mark with water, well shaken and a convenient volume of the solution withdrawn with a pipette and treated as has been already described. If the quantity of arsenic be small, the entire solution of the alkaline arseniate is taken for analysis. The volume in this case should be equal to about 100 cc.

When rapidity and not extreme accuracy is demanded, the preliminary oxidation with nitric acid as well as the subsequent evaporation of the acidified filtrate can be dispensed with. If, however, the preliminary oxidation be neglected, it will be necessary, unless the percentage of arsenic in the substance be relatively small, to employ a porcelain, iron or nickel crucible for fusion. Porcelain crucibles are never desirable, owing to the fact that the fused alkalies soon eat their way completely through the bottom. I have never been able to use a porcelain crucible for more than

[1] Since acetate of sodium serves in a remarkable manner to promote the separation of the arseniate of silver, it might be well to substitute acetic for nitric acid. See Charles E. Avery, Sill. Am. J. [2], **47**, 25.

two or three determinations. Little wrought-iron crucibles of the size and shape of the ordinary platinum crucible are very convenient and serve the purpose well, when mere estimations of arsenic are under consideration. Nickel crucibles would, doubtless, prove quite practical, but I have thus far had no experience in using them. Rose says that platinum crucibles are seriously damaged by the joint action of the molten alkali arseniates and the gas of the lamp. Fresenius appears to share Rose's opinion. My experience has been that the crucibles suffer to a far less degree than was formerly supposed. I have used a little platinum crucible over and over again for the fusion of ores, some of which have contained as much as 50 per cent. arsenic, but it does not appear to have undergone any definite injury. When an ore is rich in arsenic I generally use 0.1–0.25 gram; sometimes, however, as much as 1.0 gram is taken for analysis. There is, indeed, an action of the alkali upon the platinum, but, taking everything into consideration, it is insignificant. A crucible, before the fusion of 0.25 gram nickel speiss containing 51.25 per cent. arsenic, weighed 21.2620 grams and, after fusion, 21.2608. The difference is 0.0012 gram. Even carbonates of the alkalies attack platinum to this extent. Dr. L. de Koninck[1] found that a crucible in which he had fused 6 grams potassium sodium carbonate lost 0.001 gram.

I have selected the following examples from a large number of analyses, inasmuch as they seem peculiarly suited for giving the practical chemist a general idea as to the most convenient quantities of material to be taken for analysis, as to the volumes of $\frac{1}{10}$ normal thiocyanate to be expected, and as to the agreement of duplicate tests.

I.—*Lead Matte.*[2]

	Grams Substance.	Cc. $\frac{1}{10}$ Normal KCNS.	Per cent. As.
1	0.9983	7.3	1.83
2	0.9980	7.4	1.85

II.—*White Iron.*[2]

	Grams Substance.	Cc. $\frac{1}{10}$ Normal KCNS.	Per cent. As.
1	1.0023	25.35	6.32
2	1.0075	26.0	6.45

III.—*Lead Speiss.*[2]

	Grams Substance.	Cc. $\frac{1}{10}$ Normal KCNS.	Per cent. As.
1	0.9985	38.7	9.71
2	0.9974	38.4	9.63

[1] Zeits. für analy. Chem. **18**, 569.

[2] Analysed by Mr. J. W. Phillips.

IV.—*Nickel Speiss.*

1.0 gram was oxidised, fused, and extracted with hot water; the solution was filtered into a 500 cc. flask, acidified with nitric acid, boiled, cooled, and diluted to the mark. The flask was well shaken and for each estimation 50 cc. taken.

	Cc. Solution.	$\frac{1}{10}$ Normal KCNS.	Per cent. As.
1	50	20.55	51.36
2	50	20.45	51.12
3	50	20.45	51.12
4	50	20.50	51.25

1.0 gram speiss + 0.3 gram Sb_2O_3 was oxidised, fused, and extracted with hot water; the solution was *cooled*, filtered into a 500 cc. flask, acidified with a little nitric acid, boiled, cooled, diluted to the mark and well shaken. When the liquid had cleared the following determinations were made:

Volumetrically.

	Cc. Solution.	$\frac{1}{10}$ Normal KCNS.	Per cent. As.
1	50	20.5	51.25
2	50	20.45	51.12

Gravimetrically.

Cc. Solution.	Grams Ag_3AsO_4.	Per cent. As.
50	.317	51.35

The .317 gram Ag_3AsO_4 was dissolved in nitric acid and titrated. I used 20.5 cc. $\frac{1}{10}$ normal KCNS = 51.25 per cent. As.

These determinations show conclusively that antimony is without influence. By far the greater portion remains behind with the metallic oxides as sodium metantimoniate. The very small amount which goes into solution is precipitated by the nitric acid and, upon permitting the liquid to stand, separates as a heavy white powder. 50 cc. of the above solution were mixed with 5 cc. strong sulphuretted hydrogen water. The liquid remained perfectly clear and limpid for at least five minutes. The subsequent appearance of a faint opalescence, which gradually increased in intensity, plainly indicated a reduction of arsenic from the maximum to the minimum state of oxidation. Had even a trace of antimony been present, it should have been immediately precipi-

tated by the sulphuretted hydrogen. Numerous examples could be given showing that antimony exerts no influence, but these determinations will doubtless suffice.

Certain acid-forming oxides, such as those of phosphorus, molybdenum and vanadium, interfere with the determination of the arsenic. If any or all of these oxides be present, the arsenic must be precipitated as sulphide, then oxidised and fused.

In laboratories where large numbers of arsenic determinations are being constantly made, Mr. Pearce's volumetric modification of the Reich method will be found most practical; in laboratories, however, where there is only occasionally a demand for an arsenic determination, the author's gravimetric modification will prove most convenient.

In closing I should like to suggest that, while due allowance be made for the modifications, this silver process be henceforth known as the Reich method for determining arsenic.

JOHN C. GREEN SCHOOL OF SCIENCE, PRINCETON, N. J., *March* 1, 1886.

Communication from the Chemical Laboratory of Rutgers College.

XIII.—ON DINITROSULPHOCYANBENZENE.

BY PETER T. AUSTEN AND FRANKLIN S. SMITH.

Clemm[1] found that when trinitrochlorbenzene was treated with potassium sulphocyanide an energetic action ensued and a well-characterised compound was formed. He was unable, however, even after a number of analyses, to assign any satisfactory formula to this substance.

It appeared probable that the dinitro-derivative would be less likely to cause the formation of secondary reactions, and, if this were the case, a dinitrosulphocyanbenzene would be created. It was found on experiment that the reaction did take place easily and in quite quantitative relations.

[1] Journ. prakt. Chem. [2], **1**, 145.

Dinitrobrombenzene was dissolved in methyl alcohol, and about half its weight of potassium sulphocyanide added. The flask was placed on a water-bath and connected with a return condenser. After boiling a short time the precipitation of a yellow, crystalline sand begins, the amount of which continually increases. To avoid the excessive bumping which soon takes place, it is well, at intervals, to pour off the liquid, remove the sand, and begin the boiling anew. After an hour's boiling but little more precipitation takes place. The sand should then be removed and the liquid distilled down about one-half. On boiling the remaining liquid as before, a fresh deposit of sand will take place. In this manner a very satisfactory yield is obtained. The liquid shows a strong reaction for bromides as soon as this precipitation of the sand begins.

Dinitrosulphocyanbenzene.

The yellow sand obtained by the method just described was well washed with boiling methyl alcohol to remove any traces of the dinitrobrombenzene, and then repeatedly boiled out with water until free from bromides. When dry the substance is a fine sand, which consists of yellow, crystalline, transparent grains. It is moderately soluble in boiling chloroform, which is the best solvent which we have yet been able to find for it. Crystallised from chloroform it forms buff-yellow, small, hard, transparent crystals fusing at 139°.

Analysis:

$C_6H_3(NO_2)_2SCN$.	Calculated.	I.	II.
C	37·33	37·12	37·43
H	1·33	1·51	1·37
N	18.66	18.24	18.06
S	14.22	14.43	...

The substance is reduced with difficulty by tin and hydrochloric acid. The resulting base was not examined. The substance was slowly dissolved by concentrated boiling caustic soda, but no definite compound could be isolated from the resulting solution.

Dinitrophenylmercaptan.

When dinitrosulphocyanbenzene is added to an excess of concentrated sulphuric acid and the mixture gently heated, the reaction begins and the temperature rises, while large amounts of sulphur dioxide and carbon dioxide are evolved and ammonium sulphate

is formed in the solution. The substance, which at first goes into solution in the acid, is reprecipitated. The resulting liquid and precipitate were allowed to cool somewhat and then poured carefully into a sufficient volume of cold water. The precipitate was filtered off and washed with hot water till no reaction for sulphuric acid was obtainable. As we were unable to find any solvent for this substance from which we could crystallise it (even nitrobenzene failing to give satisfactory results), we proceeded to purify by repeated extractions with boiling alcohol, and lastly with boiling chloroform. The compound obtained after drying is an impalpable, light yellow powder. It is extremely adherent to glass, which makes it rather difficult to transfer it from one vessel to another, and it is also not easy to obtain it perfectly free from moisture.

$C_6H_3(NO_2)_2SH$.	Calculated.		
C	36	35.50	35.50
H	2	2.66	2.17
N	14	14.40	...
S	16	15.57	...

The substance is insoluble in the usual solvents. Nitrobenzene dissolves small amounts of it, but we were unable to obtain it again in a crystalline condition. It dissolves easily in warm, concentrated nitric acid, and is precipitated unchanged on pouring the solution into cold water. It fuses at 195°, and on heating it deflagrates.

We were somewhat at a loss at first to understand the reaction taking place here, but on comparing it with the action of concentrated hydrochloric acid under pressure on sulphocyanbenzene,[1] the mechanism of it was at once apparent.

$$C_6H_5SCN + 2H_2O = C_6H_5SH + CO_2 + NH_3,$$
$$C_6H_3(NO_2)_2SCN + 2H_2O = C_6H_3(NO_2)_2SH + CO_2 + NH_3.$$

The evolution of sulphur dioxide is probably due to a secondary action. If the action is continued too long, or the heat is raised too high, the substance is decomposed, and the compound is not obtained.

Dinitrophenylsulphide.

When dinitrosulphocyanbenzene is added to a mixture of fuming

[1] Billeter. Ber. **7**, 1753.

nitric acid and concentrated sulphuric acid, and the whole warmed, an energetic action takes place. The resulting solution was poured into water, and the white, flocculent precipitate which separated, was washed out with boiling water and dried. It formed a grayish-white mass with a very irregular fracture. It dissolved in boiling glacial acetic acid with some difficulty, but more easily when it was well rubbed with the acid in a mortar so as to remove the adhering film of air. From this solution it crystallised in beautiful, transparent, slightly yellow needles nearly a quarter of an inch long and about as thick as a pin, forming fan and stellar aggregates and fusing at 245°.

Analysis gave—

$(C_6H_3(NO_2)_2)_2S$.	Calculated.	Found.
C	39.34	39.20
H	1.64	1.57
N	15.30	15.38
S	8.74	8.82

The substance is then dinitrophenylsulphide, $\begin{matrix} C_6H_3(NO_2)_2 \\ C_6H_3(NO_2)_2 \end{matrix}\!\!>\!S$, and is hence isomeric with the one discovered by Beilstein and Kurbatow.[1]

A LECTURE EXPERIMENT FOR SHOWING THE COMPOSITION BY VOLUME OF NITROUS AND NITRIC OXIDES.

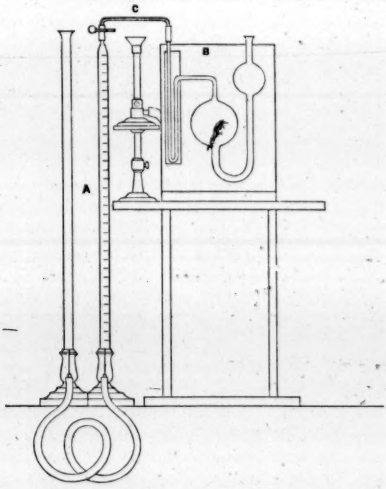
By E. H. Keiser.

The usual method of showing that nitrous oxide contains its own volume of nitrogen, and that nitric oxide contains half its volume of nitrogen, is to decompose these gases by bringing them in contact with heated potassium. For this purpose a quantity of the gas to be examined is collected in a eudiometer over mercury, and its volume is determined. The gas is then transferred to a bent glass tube closed at one end, and a small piece of potassium

[1] Ann. d. chem. Pharm. **197**, 77.

is introduced into the bent portion of the tube by passing it up through the mercury by means of a wire. The lower and open end of the tube is now closed under the mercury with the finger, and the part of the tube containing the potassium is heated with the lamp. After the combustion the tube is allowed to cool. The gas, which now consists of nitrogen, is transferred back again to the eudiometer, and its volume is determined. To perform this experiment successfully, considerable skill in the manipulation of gases is necessary, and it requires so much time that it is not adapted to the purposes of the lecture table.

The same object may be attained much more easily and rapidly by means of the simple apparatus shown in the cut. It is based upon the fact that heated metallic copper combines with all the oxygen of the nitrogen oxides and sets the nitrogen free. The method of using the apparatus is very simple, and requires but little explanation. *A* represents a gas burette for measuring the volumes of the gases. *B* is a gas pipette, which is filled with water.



The connecting tube *C* is made of hard glass and is 3 mm. internal diameter, and from 10 to 12 cm. long. It is completely

filled with granular metallic copper, which has been obtained by the reduction of the granular oxide in a current of hydrogen. The copper is held in place by plugs of asbestos in each end of the tube. To decompose the oxides of nitrogen, this tube is heated to a red heat with a Bunsen burner, and to prevent it from bending, a piece of wire gauze is wrapped around the outside and secured by wires.

A measured quantity of nitrous or nitric oxide contained in the burette *A* is passed over the heated copper by opening the pinch-cock and raising the reservoir tube of the burette. When the reservoir tube is lowered, the gas is drawn back from the pipette. It now consists of nitrogen, and its volume may be readily determined. If nitric oxide has been used, the volume of nitrogen obtained will be exactly one-half the original volume of the gas, while in the case of nitrous oxide the volume of nitrogen will be the same as the volume of nitrous oxide taken, although the copper will have been oxidised and the gas will have lost its power of supporting combustion. The error rarely exceeds .1 per cent. in the case of nitric oxide, while with nitrous oxide equally good results are obtained if the water in the burette has been previously saturated with the gas.

It is of course necessary to have the oxides of nitrogen free from air. The burette may be conveniently filled with pure nitric oxide as follows: Into a flask of about 300 cc. capacity there is placed a mixture of 100 grams of ferrous sulphate and 12 grams of potassium nitrate. To this is added a quantity of dilute sulphuric acid, obtained by mixing 60 cc. of the concentrated acid with 160 cc. of water. The flask is closed with a one-hole rubber stopper, through which passes a glass tube bent at right angles. On heating the mixture contained in the flask pure nitric oxide is evolved. A T tube is then attached to the gas burette, and one of its branches is connected with the outlet tube of the flask. The air in the burette is expelled by opening the pinch-cock and raising the reservoir tube until water flows out of the open end of the T tube. After all the air has been expelled from the generating flask the open end of the T tube is closed with a rubber tube and pinch-cock, and the gas allowed to pass into the burette.

The same apparatus serves for filling the burette with nitrous oxide, the gas in this case being made by heating pure ammonium nitrate.

BRYN MAWR, PA., *February*, 1886.

SUBSTITUTION PRODUCTS OBTAINED FROM SALICYLIC ACID.

By Edgar F. Smith and E. B. Knerr.

The mono- and di-halogen substitution products of salicylic acid have been pretty thoroughly studied, so that it may seem unnecessary to carry investigation any further in that direction. We have, however, obtained several new di-halogen acids and their derivatives by introducing two different halogen atoms into salicylic acid. These are of interest, and below we give one of these acids, reserving the others for a future communication.

1. *Meta-chlor-iodo-salicylic acid*, $C_6H_3(OH)Cl.I.COOH$.—This acid we obtained from the chlorsalicylic acid melting at 172° C. We first endeavored to prepare it by dissolving the chlorsalicylic acid in alcohol and adding the calculated amount of iodine. In one instance heat was applied to the solution. After standing for several hours the alcoholic liquid was transferred to a porcelain dish and evaporated to dryness. The residual mass was converted into the barium salt, which separated from the concentrated aqueous solution in arborescent crystals, resembling those of barium dichlorsalicylate. The salt was recrystallised and then analysed.

.1235 gram air-dried salt, heated to 160° C. for two hours, lost .0112 gram H_2O, equivalent to 9.06 per cent. H_2O.

The found $BaSO_4$ equalled .0373 gram Ba = 17.73 per cent. Ba.

An analysis of a barium salt obtained in the same manner, but at another time, gave a like result. These results point to the conclusion that the salt analysed was that of a chlor-iodo-benzoic acid, and not the barium salt of chlor-iodo-salicylic acid.

Barium chlor-iodo-benzoate, $(C_6H_3Cl.I.COO)_2Ba + 4H_2O$, requires 17.70 per cent. Ba and 9.30 per cent. H_2O. We found 17.73 per cent. Ba and 9.06 per cent. H_2O. The acid from the salt mentioned above is quite soluble in boiling water. It forms curved needles, melting at 210°C.

By pursuing the method recommended by Weselsky[1] for the introduction of iodine into aromatic compounds—viz.: the addition of mercuric oxide together with iodine to the alcoholic solution of chlorsalicylic acid, the chlor-iodo acid was obtained easily and in

[1] Ann. **174**, 99.

good quantity. The reaction was aided by a gentle heat, and when completed, the alcoholic solution was evaporated to dryness, the residue boiled up with an excess of sodium carbonate, and the liquid filtered. The discolored filtrate was acidified with hydrochloric acid and the acid, which separated, was filtered off, washed, and converted into a barium salt. The latter separated from its concentrated aqueous solution in bundles of needles having a pink color. This salt was recrystallised six times. The acid from it was also recrystallised a number of times, and its melting-point tested on each occasion. It melted regularly at 224° C., with slight decomposition. The acid is difficultly soluble, even in boiling water. From a mixture of hot water and alcohol it separates in long, colorless needles. Ferric chloride imparts a violet coloration to its solutions. After proving the presence of both iodine and chlorine qualitatively, the acid was burned, together with lead chromate.

.3080 gram dried acid gave .0852 gram carbon = 27.66 per cent. C, and .0059 gram hydrogen = 1.59 per cent. H.

The acid $C_6H_2(OH)Cl.I.COOH$ requires 28.13 per cent. carbon and 1.34 per cent. hydrogen.

Theoretically, this acid contains 42 per cent. of iodine, and in its combustion, as well as in that of the ethyl ester (see below), this high iodine content gave us trouble, as free iodine invariably escaped from the combustion tube and settled in the calcium chloride tube. To obviate this we resorted to the following expedient: after filling the tube with a long layer of lead chromate we placed upon the latter a wad of asbestos, following this with a layer of the same material charged with metallic silver, which we deposited by the electric current. The silvered asbestos was heated, and effectually prevented the iodine vapors from entering the calcium chloride tube. A layer of metallic silver (from the oxide) answered the same purpose.

Salts of Chlor-iodo-salicylic Acid.

Sodium Chlor-iodo-salicylate, $C_6H_2(OH)Cl.I.COONa + 2H_2O$, was made by boiling the acid with sodium carbonate. It is soluble in water and crystallises from the same in beautiful, flat, shining needles, which in several instances exceeded an inch in length.

Analysis: .1607 gram air-dried salt lost on heating to 150° C. for several hours, .0184 gram H_2O = 10.76 per cent., equivalent to

2 mols. The sodium sulphate weighed .0315 gram = .0102 gram Na, equivalent to 6.34 per cent. Na. Theory requires 10.09 per cent. H_2O and 6.45 per cent. Na.

Calcium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Ca + 5H_2O$.—This salt consists of beautiful pink needles. It is much more soluble in water than the corresponding barium salt.

Analysis: Found 13.32 per cent. H_2O and 5.54 per cent. Ca. Required 12.41 per cent. H_2O and 5.51 per cent. Ca.

Barium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Ba + 4\frac{1}{2} H_2O$.—It occurs in long pink needles, rather difficultly soluble in water.

Analysis: .1582 gram salt lost, at 180° C., .0151 gram water = 9.54 per cent., or $4\frac{1}{2}$ mols. The $BaSO_4$ equalled .0436 gram = .0256 gram Ba, or 16.18 per cent. Required 9.96 per cent. H_2O and 16.83 per cent. Ba.

Magnesium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Mg + 5\frac{1}{2}H_2O$.—Pink leaflets, quite soluble in hot water. Its analysis gave the following:

.4023 gram substance heated to 135° C. to constant weight lost .0558 gram = 13.87 per cent. H_2O, equivalent to $5\frac{1}{2}$ mols.

The magnesium which was found equalled 3.83 per cent. Theory requires 13.78 per cent. H_2O and 3.87 per cent. Mg.

Zinc Chlor-iodo-salicylate, $(C_6H_2(OH)I.Cl.COO)_2Zn + 3H_2O$. —Beautiful white needles, grouped together in clusters. It is quite readily soluble in hot water.

Analysis: .1888 gram substance lost .0144 gram when heated to 130° C. This is equivalent to 7.62 per cent. H_2O, or 3 mols.

The quantity of ZnO equalled .0214 gram = .0170 gram Zn or 9.00 per cent. Zn. Theory requires 7.57 per cent. H_2O and 9.10 per cent. Zn.

The following salts were prepared, but not analysed: the *potassium* salt, forming reddish-brown, matted needles, quite soluble in water; the *manganese* salt, consisting of chocolate-brown monoclinic needles, readily soluble in water; the *cadmium* salt, appearing in pink needles, which are rather soluble; the *silver* salt, forming an amorphous, yellow, insoluble powder; and the *copper* salt, consisting of bluish-green soluble needles.

Esters of Chlor-iodo-salicylic Acid.

The *methyl ester*, $C_6H_2.OH.Cl.I.CO.O.CH_3$, was prepared by heating the silver salt with alcoholic methyl iodide in a flask pro-

vided with a return cooler. The compound separated from its concentrated alcoholic solution in flat, broad needles, melting at 129°–130° C.

The *ethyl ester*, $C_6H_2.OH.Cl.I.CO.O.C_2H_5$, forms white plates, readily soluble in hot alcohol. It was analysed as indicated under the acid.

Analysis : .1427 gram dry substance gave .0475 gram carbon = 33.28 per cent. C, and .0044 gram H = 3.08 per cent. H. Theory requires 33.07 per cent. C and 2.45 per cent. H.

Some years ago a dichlorsalicylic acid was prepared by one of us (S.). At that time but one acid of this description was known.[1] The acid of Rogers melted at 223°–224°, while the one obtained by us melted at 213°–214° C. Points of difference in various salts were also observed, so that a number of these, as well as other derivatives, were made and analysed.[2] We have had occasion to repeat our work with the dichlor-acid, and have gotten results agreeing with those obtained at first. The melting-point of the acid has been repeatedly tested and found to be 213°–214°. This acid we have endeavored, by various ways, to convert into a dichlor-nitro-salicylic acid, but have not succeeded. The first attempt was made by dissolving the dichlor-acid in a cooled mixture of equal parts of fuming nitric acid and glacial acetic acid. On pouring the solution into water a yellow-colored mass separated. This was filtered, washed with cold water, and then converted into a barium salt. As the aqueous solution cooled the salt separated out in orange-colored needles. It dissolved with difficulty, even in hot water. After several crystallisations it was analysed.

.1626 gram air-dried salt lost, at 180° C., .0088 gram H_2O = 5.41 per cent.; the $BaSO_4$ weighed .0645 gram = .0379 gram Ba, or 23.30 per cent. Ba.

These results indicate a dichlornitrophenol. The free phenol from the above salt is very difficultly soluble in hot water. It volatilises with steam and crystallises in yellow-colored leaflets melting at 122° C. By reference to the first edition of Beilstein's Org. Chemie, p. 1022, it will be noticed that three phenols of the

[1] Rogers, Inaugural Diss. Goettingen, 1875. [2] Beilstein's Organische Chemie, Erste Aufl.

constitution indicated by the above analysis exist, and that the 1, 2, 4, 6-body melts at 121°–122° C., forms yellow leaflets, and further, that its barium salt consists of bundles of orange-red needles, difficultly soluble in water. The salt also contains two mols. of H_2O. Our salt fully agrees with all these properties. The potassium salt obtained by us formed chrome-red, anhydrous, flat needles. This, too, agrees with the potassium salt of the 1, 2, 4, 6-phenol.

Our other attempts to introduce the nitro-group into the dichlor-acid were made by taking, first, two parts of glacial acetic acid and one part nitric acid; second, by conducting the vapors from lead nitrate into a glacial acetic acid solution of the acid; and third, by leading the gas evolved from the action of nitric acid and arsenious acid into an ethereal solution of the dichlor-acid. The principal product in all these experiments was the dichlor-nitrophenol melting at 122°.

Upon fusing dichlorsalicylic acid with potassium hydroxide we obtained a product which in many respects indicated gallic acid. The true position of the second atom of chlorine in the dichlor-acid melting at 213°–214° has never been definitely determined.

Action of the Gas from As_2O_3 *and* HNO_3 *upon Wintergreen Oil.*

At the suggestion of one of us (S.) Mr. A. F. Linn, formerly of this laboratory, rectified a quantity of commercial wintergreen oil, and, after dissolving a portion of the purified product in ether, conducted the gas obtained from arsenious oxide and nitric acid into the ethereal solution, until it had assumed a deep reddish-brown color. The vessel containing the mixture was cooled as long as the gas was introduced, but then tightly corked and gently warmed upon a water-bath for a brief period, after which it was allowed to stand. In the course of a few hours a mass of crystals separated. These were removed and, after being freed of adhering oil, were digested with hot ether. It was soon observed that a part of the crystalline mass was exceedingly insoluble in the solvent employed. This suggested treating the compound, finely divided, first with cold ether. By this procedure the original product was resolved into two portions, the one quite readily soluble in cold ether, the other only soluble in this reagent when it was applied warm and in considerable quantity. The soluble compound, after a number of crystallisations, showed the constant melting-point

94°. It forms long, white needles. For convenience we will designate it *A*. The insoluble derivative, which we will call *B*, crystallised from ether in octahedral forms, exhibiting a beautiful play of colors. It melted at 118° C. At this point Mr. Linn discontinued the work. We have since obtained the same compounds, and our first step was to expose them to the action of boiling alkaline hydroxides. After treating *A* several hours with potassium hydroxide its cold solution was acidified with hydrochloric acid, which caused the separation of a white, flocculent mass. This was filtered, washed with cold water, and then converted into a barium salt. A portion of the free acid melted at 227°–228° C. Its fusion at this temperature, and the manner in which it had been obtained, led to the suspicion that the acid was, in all probability, *a*-metanitrosalicylic acid (m. p. 228° C.)[1] We therefore set free all the acid from the barium salt and converted it into the corresponding calcium salt. This we obtained in long, delicate, silky needles. It was analysed.

.1340 gram air-dried salt lost, at 180° C., .0276 gram water, or 20.58 per cent. H_2O.

The $CaSO_4$ found weighed .0358 gram, equivalent to .0104 gram Ca = 9.77 per cent. Ca.

This salt is very readily soluble, even in cold water. By reference to the articles already cited it will be discovered that the properties of the salt analysed by us agree perfectly with those of the calcium salt of *a*-metanitrosalicylic acid, and that the analysis just given agrees with the theoretical requirement of the salt $(C_6H_3(NO_2)OH.COO)_2Ca + 6H_2O$. The free acid gave a deep blood-red color with ferric chloride; this is also a characteristic of the nitrosalicylic acids. As already observed, the acid melted from 227°–228° C. The compound affording the *a*-nitro-acid melted at 94° C. Assuming this to be the ethyl ester of the acid, it will be noticed, on reference to Wattenberg's thesis, that the ethyl ester prepared by him melted at 93° C.; further, that the properties of the two compounds are identical. They are doubtless the same.

The insoluble product *B* was likewise boiled with potassium hydroxide. The acid from it appeared to be more soluble than the acid derived from *A*. It was, however, converted into its barium salt. This crystallised in rather large, yellow-colored

[1] Wattenberg's Inaugural Dissert. Goettingen, 1875; and Ann. **195**, 9.

needles from its dilute aqueous solution. An analysis of the salt gave the following:

.1708 gram air-dried salt suffered no loss on heating it to 150° C. for several hours. Evaporated to dryness with sulphuric acid it gave .0788 gram $BaSO_4$ = .0463 gram Ba = 27.10 per cent. Ba.

This agrees with the requirements of an anhydrous barium nitrosalicylate, which demands 27.20 per cent. Ba. The salt corresponds to that described by Hall.[1] The acid, after several crystallisations, melted at 125° C., and when anhydrous, at 144° C., proving conclusively that it was *β*-metanitrosalicylic acid. Ferric chloride imparted a blood-red coloration to its aqueous solution. The compound *B* melting at 118° C. we have not investigated farther.

The production of the two isomeric nitrosalicylic acids by the above method is new, so far as we are aware; hence this detailed account.

WITTENBERG COLLEGE, SPRINGFIELD, OHIO, *March* 2, 1886.

ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[2]

PART IV.

BY W. H. PERKIN, Jun., *Privatdocent at the University of Munich.*

(Continued from p. 372, Vol. 7.)

Dehydrobenzoylacetic Acid.

Among the many reactions in which ethylic acetoacetate takes part, there are few more interesting than the condensation which this body undergoes on prolonged boiling; by this treatment two molecules appear to combine, with elimination of two molecules of alcohol and formation of dehydracetic acid, according to the equation—

$$2CH_3.CO.CH_2.COOC_2H_5 = C_8H_8O_4 + 2EtOH.$$

This acid, the constitution of which, in spite of many experiments,

[1] Dissertation, Goettingen, 1875; and Ann. **193**, 31. [2] Communicated by the Author.

still remains to be explained, was first obtained by Geuther[1] by passing carbonic anhydride over the heated sodium derivative of ethylic acetoacetate. During the reaction a quantity of ethylic acetoacetate distils over, and the sodium salt of dehydracetic acid remains in the retort. On dissolving the latter in water and acidifying with dilute sulphuric acid the acid is set free, and by repeated recrystallisation from water, can easily be obtained pure in colorless leafy crystals melting at 109°.

Geuther proved this compound to be a monobasic acid, forming salts of the formula $C_8H_7O_4M$. At a more recent date Oppenheim and Precht[2] undertook the further investigation of the acid, and succeeded in preparing a number of derivatives, which they carefully examined, and from the results proposed the following as the most probable constitutional formula:

$$CH_3.CO.CH.C\begin{matrix}C(COOH)\\ \diagup\!\!\diagdown\\ C(OH)\end{matrix}\!\!>CH.$$

This formula presupposes that in the formation of this acid from two molecules of the acetoacetate, the methyl-group of one molecule takes part in the reaction, whereas the methyl-group of the second molecule remains intact. In order to test the accuracy of this formula it appeared interesting to determine whether it would be possible under the same conditions to obtain a similar body from ethylic benzoylacetate, in which case the two phenyl-groups would be excluded from taking part in the condensation.

The constitution of an aromatic compound of this kind would probably be much easier to determine, and if it were found that its derivatives behaved in a way exactly analogous to those of dehydracetic acid itself, it would be legitimate to suppose that the methyl-groups of the two molecules of ethylic acetoacetate which went to form dehydracetic acid did not take part in the reaction.

In the first experiments on ethylic benzoylacetate it was noticed that in distilling this body rapidly a great part went over as a colorless oil, a considerable quantity of a black tarry mass being left behind, partly soluble in carbonate of soda solution on continued agitation. On filtering and acidifying the alkaline solution an acid was deposited in the form of brownish flakes; this by repeated recrystallisation from alcohol was obtained pure in the form of long yellow needles. As it was thought possible that this might be the desired acid, numerous experiments were made in order to find

[1] Zeitschrift für Chemie, 1866, 8. [2] Berichte **9**, 324, 1100.

some means of obtaining it in larger quantity. The following process was found to give the best results:

Ethylic benzoylacetate was first heated to boiling in portions of 10–15 grams in test-tubes or small retorts for 7–8 minutes, during which operation the mass gradually became darker, whilst a quantity of lower boiling oil was given off; this was collected for further examination. On cooling, the residue generally solidified to a brownish cake of crystals. The distillate from a number of such operations was first examined. On fractioning, the principal portion passed over between 70° and 110°, then the thermometer rose rapidly to 180°, between which temperature and 210° a considerable quantity distilled; a small residue was left, which appeared to consist in great part of unchanged ethylic benzoylacetate. The fraction 70°–110°, which had a strongly acid reaction, was mixed with dry carbonate of potash, and after remaining for some time, distilled on a water-bath. On further fractioning, the distillate went over almost to the last drop between 78° and 80°, and possessed all the properties of common alcohol. The residual potash salt was then acidulated with dilute sulphuric acid and distilled in steam; a strongly acid liquid passed over, which showed all the reactions of acetic acid. The fraction 70°–110° was therefore a mixture of alcohol and acetic acid.

On refractioning the fraction 180°–210°, nearly the whole distilled over between 190°–200°, and was from its odor easily recognised as acetophenone. This was confirmed by warming it with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide, when a copious precipitate of indigo was slowly formed.

The solid residue from these experiments was then boiled for a considerable time with alcohol and animal charcoal, and filtered, the new acid crystallising out in long yellow needles on cooling. On distilling off the alcohol from the mother-liquor of these crystals it deposited a quantity of a dark brown oil; on heating this again in the way described above, it gave a new quantity of acid. This treatment was repeated until the residual oil on further heating no longer solidified on cooling, but remained behind as a blackish tarry mass, which, however, still contained considerable quantities of the acid. In order to extract this, the whole was dissolved in a little alcohol, enough potash added to neutralise the acid, the product diluted with water, and several times extracted with ether. On acidifying the solution of the potash salt, the acid

was deposited in a crude state, and was treated with alcohol and animal charcoal as described above.

The different crops of crystals were then mixed together, crystallised several times from alcohol, and thus obtained pure. The analysis gave the following numbers:

I. 0.1879 gram substance gave 0.0715 gram H_2O and 0.5082 gram CO_2.

II. 0.2577 gram substance gave 0.0958 gram H_2O and 0.6978 gram CO_2.

III. 0.1941 gram substance gave 0.0746 gram H_2O and 0.5241 gram CO_2.

IV. 0.1974 gram substance gave 0.0740 gram H_2O and 0.5319 gram CO_2.

	Found.				Theory, $C_{18}H_{12}O_4$.
	I.	II.	III.	IV.	
C	73.76	73.85	73.64	73.49 per cent.	73.97 per cent.
H	4.22	4.13	4.27	4.16	4.11
O	22.02	22.02	22.09	22.35	21.92

This substance, for which I propose the name dehydrobenzoylacetic acid, has therefore the formula $C_{18}H_{12}O_4$, and is formed from two molecules of ethylic benzoylacetate in a way exactly analogous to the formation of dehydracetic acid from ethylic acetoacetate, according to the equation—

$$\underset{\text{Ethylic benzoylacetate.}}{2C_6H_5.CO.CH_2.COO.C_2H_5} = \underset{\text{Dehydrobenzoylacetic acid.}}{C_{18}H_{12}O_4} + 2C_2H_5.OH.$$

This acid crystallises from its solution in hot alcohol in long yellow needles which melt at 171°–172°. It is moderately soluble in hot alcohol, but only sparingly in the cold. On the addition of a drop of ferric chloride to the hot alcoholic solution it gives a deep orange-red coloration. Dehydrobenzoylacetic acid dissolves easily in benzene, chloroform, bisulphide of carbon and ether, but sparingly so in light petroleum. On evaporating these solutions the acid crystallises out beautifully in long yellow needles. The solution in bisulphide of carbon does not decolorise bromine in the cold, and only very slowly on boiling, hydrogen bromide being given off. This behavior is exactly analogous to that of dehydracetic acid, which, when treated with bromine, forms a substitution-product, $C_8H_7O_4Br$, and not an additive product, as might be expected, considering the small percentage of hydrogen which the acid contains.

Dehydrobenzoylacetic acid dissolves in concentrated sulphuric acid with an olive-green color; on warming, a beautiful violet solution is obtained, which, when examined with the spectroscope, gives exactly the same absorption-spectrum as indigo.

The acid is not acted on, even by prolonged heating with acetic anhydride, being precipitated unchanged on adding water, a proof that the dehydrobenzoylacetic acid contains no hydroxyl-groups.

The acid chars when submitted to dry distillation, a quantity of gas being given off; but if heated with soda-lime, acetophenone is formed.

Dehydrobenzoylacetic acid readily combines with phenylhydrazine, forming an intensely yellow compound, which is difficult to purify, and has not as yet been analysed. The pure acid dissolves easily in ammonia, soda and sodic carbonate, forming yellow solutions.

The ammonium salt was obtained in the usual way, by allowing the solution of the acid in ammonia to stand over sulphuric acid in a vacuum until the excess of alkali had been removed. The following salts were prepared by precipitation: Silver nitrate causes the precipitation of the silver salt as a yellowish-white flocculent mass, which is very stable and only slowly acted on by light. It was collected, well washed with water, dried at 100°, and analysed with the following result:

0.2949 gram substance gave 0.0818 gram H_2O, 0.5874 gram CO_2 and 0.0786 gram silver.

	Found.	Theory, $C_{18}H_{11}O_4Ag$.
C	54.32 per cent.	54.19 per cent.
H	3.08	2.75
Ag	26.65	27.00
O	15.95	16.06

Dehydrobenzoylacetic acid is therefore a monobasic acid. The *ferric salt* is thrown down as a beautiful scarlet precipitate on adding ferric chloride to a solution of the ammonium salt. Ferrous sulphate, on the contrary, gives a blackish-violet precipitate, the behavior with these two reagents being a very characteristic reaction for the acid. The *copper salt* is obtained, on adding cupric sulphate, as a light greenish precipitate, soluble in ammonia. The *lead*, *calcium*, *barium*, *zinc* and *tin salts* are heavy white precipitates, almost insoluble in water. *Nickel sulphate* gives, with a solution of the ammonium salt, a light green almost colorless

precipitate, soluble in ammonia. All these salts are extremely stable.

If ethylic benzoylacetate is boiled as described above for about eight minutes, the only condensation-product formed in any quantity is dehydrobenzoylacetic acid. If, however, the boiling is continued for a longer time, the reaction becomes more and more complicated, higher condensation-products being formed.

In order to study these, and, if possible, to determine their constitution, the ethylic benzoylacetate was heated in small retorts in quantities of from 10 to 15 grams for about half an hour, during which time alcohol and acetophenone were given off continuously and fairly regularly. The black tarry residue, which became semi-solid on cooling, was found to contain at least two condensation-products besides dehydrobenzoylacetic acid; these were separated as follows: In order to remove the dehydrobenzoylacetic acid the mass was first treated with a moderately concentrated solution of ammonia and allowed to stand, the whole being well stirred from time to time. After filtering off the aqueous solution of the ammonium salt the residue was well washed with water, and then several times extracted with hot alcohol; this removed all the coloring matter, and left a yellowish amorphous mass, which will be described further on.

The dark brown alcoholic solution was digested for a long time with animal charcoal, filtered, and the bulk of the alcohol distilled off. On cooling, a beautifully crystalline body separated, which was purified by repeated recrystallisation.

The analysis gave numbers agreeing with the formula $(C_9H_6O_2)_x$.

I. 0.2343 gram substance gave 0.0941 gram H_2O and 0.6374 gram CO_2.

II. 0.1746 gram substance gave 0.0709 gram H_2O and 0.4722 gram CO_2.

	Found.		Theory, $(C_9H_6O_2)_x$.
	I.	II.	
C	74.19	73.76 per cent.	73.97 per cent.
H	4.41	4.51	4.11
O	21.40	21.73	21.92

This compound probably has the formula $C_{27}H_{18}O_6$, being formed from three molecules of ethylic benzoylacetate by the elimination of three molecules of alcohol, according to the equation—

$$3C_6H_5.CO.CH_2.COO.C_2H_5 = C_{27}H_{18}O_6 + 3C_2H_5.OH.$$

This substance melts at 273°–275°. It is sparingly soluble in cold alcohol, more easily in hot, and crystallises on cooling in beautiful silky plates, which strongly resemble anthracene, and give a beautiful play of colors with polarised light. It is almost insoluble in benzene, light petroleum and acetone. In ether and carbon bisulphide it is somewhat soluble, and on evaporation crystallises in glittering plates. The solution in carbon bisulphide is only very slowly acted on by bromine, hydrogen bromide being given off. On adding an ethereal solution of sodium ethoxide to the solution of the substance in warm ether, a voluminous precipitate of a sodium compound is thrown down; this is decomposed by treatment with acids with regeneration of the original compound.

This substance, however, is not a true acid. It dissolves easily in dilute alcoholic soda or sodium ethoxide, but is entirely reprecipitated on passing carbonic anhydride, so that in this case a sodium compound corresponding with that of ethylic benzoylacetate is formed, and not the sodium salt of an acid. If the solution in alcoholic potash is allowed to remain for some time, the compound is slowly but completely decomposed. On diluting the product with water, and acidifying with dilute sulphuric acid, an acid is precipitated which has all the properties of benzoylacetic acid. It melts at 80°–85°, gives the characteristic violet coloration with ferric chloride, and is decomposed into carbonic anhydride and acetophenone on heating. This acid appears to be produced almost quantitatively by the action of potash on the substance $C_{27}H_{18}O_6$.

If it is boiled with alcoholic potash, benzoic acid, acetophenone and other bodies are formed. Heated in a test-tube the compound $C_{27}H_{18}O_6$ sublimes partly unchanged, but most of it is decomposed, with separation of oily bodies, probably acetophenone. When distilled with zinc-dust a light boiling body is given off, which burns with a strongly luminous flame, and appears to be benzene. It is not decomposed by boiling with dilute sulphuric acid. It dissolves in concentrated sulphuric acid with a faint yellowish color, which is not perceptibly changed on warming. It is easily attacked by hot concentrated nitric acid, and on adding water to the product a yellowish mass is precipitated, which crystallises beautifully from alcohol, and is probably a nitro-derivative. On

warming the compound $C_{37}H_{18}O_6$ with phenylhydrazine, it yields an intensely yellow body, which, however, was not further examined.

The yellow amorphous compound mentioned above (p. 106) as remaining when the compound $C_{37}H_{18}O_6$ was dissolved by treating the crude product with alcohol, was then further examined.

This substance melts above 300°. It is insoluble in most of the usual solvents, and can therefore be easily separated from impurities by repeated extraction with them. It is thus obtained as a light yellow amorphous mass, which gave the following numbers on analysis:

I. 0.1243 gram substance gave 0.0460 gram H_2O and 0.3380 gram CO_2.

II. 0.1556 gram substance gave 0.0586 gram H_2O and 0.4239 gram CO_2.

	Found.		Theory.
	I.	II.	$(C_9H_4O_2)_n$.
C	74.16 per cent.	74.29 per cent.	73.97 per cent.
H	4.11	4.18	4.11
O	21.73	21.53	21.92

The compound appears to be homogeneous, the above analyses having been made with two distinct preparations. It is possible that it may have the formula $C_{36}H_{24}O_8$, being a condensation-product of four molecules of ethylic benzoylacetate,

$$4C_6H_5.CO.CH_2.COO.C_2H_5 = C_{36}H_{24}O_8 + 4C_2H_5.OH.$$

It is an acid, and dissolves easily in sodium ethoxide, being reprecipitated by dilute sulphuric acid, but not by carbonic anhydride. It is also partially soluble in ammonia. On boiling it with sodium ethoxide a deep red solution is formed; this, when acidified, deposits a small quantity of an acid, the alcoholic solution of which gives a violet coloration with ferric chloride. The following is an extremely characteristic reaction of this substance. If the merest trace of it is mixed with concentrated sulphuric acid it dissolves to a yellowish solution, and on warming this the color changes slowly to a reddish-brown and then to a reddish-violet. If this solution be further heated a most intense bluish-violet coloration is produced, which becomes purple on strongly heating. The bluish-violet coloration is most beautiful, and strongly resembles methylene-blue. The color disappears on diluting with water.

Owing to the difficulty of obtaining any quantity of these last two condensation-products, I have not examined them further, but confined my attention to the dehydrobenzoylacetic acid.

Ethylic Dehydrobenzoylacetate.

In order to prepare this ethereal salt, silver dehydrobenzoylacetate was digested on a water-bath for two hours with excess of ethyl iodide and a little dry ether; in this way the salt was completely decomposed. After collecting and extracting the precipitated iodide of silver several times with ether, and evaporating the ethereal solution, a semi-solid mass was obtained, which was first spread on a porous plate to free the crystals from oily matter, and then several times recrystallised from benzene. When analysed it gave the following results:

0.1843 gram of substance gave 0.0858 gram H_2O and 0.5050 gram CO_2.

	Found.	Theory. $C_{17}H_{11}O_2.COOC_2H_5$.
C	74.73 per cent.	75.00 per cent.
H	5.17	5.20
O	20.00	20.00

This compound is therefore ethylic dehydrobenzoylacetate. It crystallises from benzene in almost colorless glittering needles which melt at 159°, and show a beautiful play of colors when examined with the polariscope. If carefully heated it appears to distil almost without decomposition.

It is moderately soluble in alcohol, acetone, benzene and bisulphide of carbon, more sparingly in ether and light petroleum. The solution in alcohol gives a reddish-brown coloration on the addition of a drop of ferric chloride. Warmed with alcoholic potash it is easily saponified, dehydrobenzoylacetic acid being generated.

Its alcoholic solution when mixed with phenylhydrazine yields an intensely yellow compound, which, however, has not yet been obtained pure enough for analysis; its formation is, however, a proof that the dehydrobenzoylacetic acid contains at least one carbonyl-group.

If an ethereal solution of ethylic dehydrobenzoylacetate is treated with an ethereal solution of sodic ethylate, an intensely yellow sodium compound is precipitated; but, unfortunately, ethylic dehydrobenzoylacetate is so sparingly soluble in ether that

it was found impossible to obtain the compound in quantity sufficient for analysis.

In the course of some experiments on dehydracetic acid, the results of which I hope to make public at some future time, it was found that the methyl salt of this acid possesses the property of forming a sodium compound of the formula $C_8H_6O_4CH_2Na$, in which one hydrogen of the methyl compound is directly replaced by sodium.

It is extremely probable, therefore, that the sodium compound of ethylic dehydrobenzoylacetate is similarly constituted.

Action of Potassic Hydroxide on Dehydrobenzoylacetic Acid.

Dehydracetic acid is, as is well known, easily split up by heating with alkalis, into acetone, acetic acid and carbonic anhydride, according to the equation—

$$C_8H_8O_4 + 3H_2O = CH_3.CO.CH_3 + 2CH_3.COOH + CO_2.$$

It appeared likely, therefore, that by treating dehydrobenzoylacetic acid in the same way, similar decomposition-products would be produced, thus affording evidence that this acid and dehydracetic acid were analogous compounds.

In order to test this the action of potash on dehydrobenzoylacetic acid was carefully studied in the following way:

The pure acid was first dissolved in dilute alcoholic potash, and after an excess of a concentrated solution of the latter had been added, the whole was heated to boiling on a water-bath for several hours. During the reaction the mass became gradually darker; when finished, the smell of acetophenone was easily recognisable.

In order to isolate the products the alcohol was first slowly distilled off, water was then added, and the whole distilled in a current of steam. The distillate, which smelt strongly of acetophenone, contained small particles of oil, which were separated from the watery liquid by shaking with ether. On evaporating the ether a colorless oil remained, which, on fractioning, went over entirely between 195°–200°, and was undoubtedly acetophenone. This was confirmed by shaking it with a solution of orthonitrobenzaldehyde in dilute soda; in a short time an indigo-blue precipitate separated in considerable quantity.

The alkaline solution which was freed from the acetophenone in the way above described was acidified with dilute sulphuric acid,

and again distilled, when an acid liquid passed over which smelt distinctly of acetic acid; the quantity, however, was so small that an analysis could not be performed. The residue in the retort was then several times extracted with ether, and on evaporating the solution, a dark-brown semi-solid acid was obtained. This was first separated from oily matter by spreading it out on a porous plate, and then recrystallised from water. In this way it was obtained in colorless needles melting at 118°–120°, and possessing all the properties of benzoic acid, with which it was undoubtedly identical.

Dehydrobenzoylacetic acid is therefore decomposed on heating with alcoholic potash into acetophenone, acetic acid, benzoic acid and carbonic anhydride, according to the equation—

$$C_{18}H_{12}O_4 + 3H_2O = C_6H_5.CO.CH_3 + CH_3.COOH + C_6H_5.COOH + CO_2.$$

The reaction is perfectly analogous to the formation of two molecules of acetic acid and one of acetone by the action of potash on dehydracetic acid.

In the course of these experiments it was noticed that when the boiling with potash was continued for a short time only, the benzoic acid obtained was always mixed with a certain quantity of another acid, the alcoholic solution of which gave a violet coloration with ferric chloride, strongly resembling that produced by benzoylacetic acid. In order, if possible, to obtain this acid in larger quantity, the action of potash on dehydrobenzoylacetic acid was tried in the cold, and it was found that it was completely decomposed if mixed with a concentrated solution of alcoholic potash and allowed to remain for twelve hours. The mass became dark reddish-brown, and in a short time a considerable quantity of a potash salt crystallised out in glittering plates. On adding water the whole dissolved, forming a reddish-brown solution, which smelt only very faintly of acetophenone. In order to isolate the products of the reaction the alkaline liquid was well cooled, acidified with dilute sulphuric acid, and once or twice extracted with ether. On allowing the ethereal solution to evaporate a quantity of a dark brownish acid was left, which was purified from oily matter by spreading it out on a porous plate, and thus obtained as a slightly yellowish, hard, crystalline mass. This was dissolved in dilute ammonia, well shaken with pure animal charcoal, and filtered. In this way an almost colorless solution of the ammonium salt was obtained,

which was acidified with dilute sulphuric acid and extracted with ether. The ethereal solution, on evaporation, deposited a faintly yellowish-colored crystalline acid; this, after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.1796 gram of substance gave 0.0841 gram H_2O and 0.432 gram CO_2.

	Found.	Theory, $C_9H_8O_3$.
C	65.62 per cent.	65.85 per cent.
H	5.23	4.88
O	29.15	29.27

This acid has, therefore, the same constitution as benzoylacetic acid, and is undoubtedly identical with it. It melted at 83°–85° (after recrystallising from benzene at 98°–100°), and exhibited all the properties of benzoylacetic acid. The solution in alcohol gives an intense violet coloration with ferric chloride, and the free acid, when distilled, is split up into acetophenone and carbonic anhydride. In order to be certain that the acid obtained from the dehydrobenzoylacetic acid really had the constitution $C_9H_8O_3$, it was converted into the silver salt, and analysed with the following result:

0.1463 gram substance gave 0.0592 gram silver.

	Found.	Theory, $C_6H_5.CO.CH_2.COOAg$.
Ag	40.36 per cent.	39.84 per cent.

There is therefore no doubt that dehydrobenzoylacetic acid, when treated with alcoholic potash in the cold, is converted into benzoylacetic acid, according to the equation—

$$C_{18}H_{12}O_4 + 2H_2O = 2C_6H_5.CO.CH_2.COOH.$$

This reaction is exactly the reverse of its formation from two molecules of ethylic benzoylacetate.

In order to determine whether this decomposition really did take place according to the above reaction, some quantitative experiments were made, and the amount of benzoylacetic acid produced weighed. 3 grams of pure dehydrobenzoylacetic acid were mixed with a concentrated solution of alcoholic potash, and allowed to stand at the ordinary temperature until a very faint smell of acetophenone was perceptible. The product was then treated as described above. After evaporating the ethereal extract of the acid formed in a weighed dish, 3.15 grams of crude product were obtained (calculated for the above equation 3.3 grams). After spreading it out

on a porous plate, and thus removing a trace of oily matter, the almost colorless acid left weighed nearly 3 grams. It was then treated with ammonia and animal charcoal, and gave 2.8 grams of nearly pure benzoylacetic acid.

In order to be sure that this acid was benzoylacetic acid it was heated in a retort until the whole was decomposed, and the resulting oil dissolved in ether and shaken with a dilute solution of sodic hydroxide. On acidifying the alkaline solution and extracting with ether, a very small quantity of benzoic acid was obtained. The neutral oil formed by the decomposition showed the boiling-point of 195°, and was undoubtedly acetophenone. It is probable, therefore, that on boiling dehydrobenzoylacetic acid with potash benzoylacetic acid is first formed, which is then further decomposed into benzoic acid, acetic acid, acetophenone and carbonic anhydride.

Reduction of Dehydrobenzoylacetic Acid.

Dehydrobenzoylacetic acid, $C_{18}H_{12}O_4$, besides the carboxyl-group, contains two atoms of hydrogen, one of which at least must be present in the ketone form, CO, from the fact that the acid combines with phenylhydrazine. This phenylhydrazine compound could be obtained crystalline only with difficulty, and then in such small quantity that a complete analysis could not be made, but only a nitrogen determination, which seemed to show that the body had the formula $C_{18}H_{12}O_3.N_2H.C_6H_5$, one molecule of the acid combining with one molecule of phenylhydrazine. In order to obtain some idea as to the condition of the fourth oxygen-atom in the molecule $C_{18}H_{12}O_4$, it was next treated with reducing agents under different conditions, the best results being obtained with sodium amalgam in the following way :

Dehydrobenzoylacetic acid was dissolved in dilute sodic hydroxide and an excess of liquid sodium amalgam slowly added, the whole being well cooled during the operation, and the product allowed to stand for twenty-four hours in order to ensure complete reduction.

At first no evolution of hydrogen was perceptible, but towards the end of the reaction a quantity of gas was given off and a small amount of a resinous body formed, which was filtered off from the alkaline solution, but was too small for further examination. On acidifying the filtrate with dilute sulphuric acid it deposited an almost colorless amorphous acid, which was collected, well washed

with water and spread out on a porous plate to free it from traces of oily matter. This crude product was dissolved in a little boiling benzene and then light petroleum boiling at 70°–80° added until a slight turbidity was produced. On standing, this solution deposited a quantity of a new acid in colorless plates, which were obtained pure by recrystallisation from benzene and light petroleum.

The analysis gave the following numbers:

I. 0.1665 gram substance gave 0.0761 gram H_2O and 0.4750 gram CO_2.

II. 0.1485 gram substance gave 0.0669 gram H_2O and 0.4247 gram CO_2.

III. 0.1782 gram substance gave 0.0723 gram H_2O and 0.5097 gram CO_2.

	Found.			Theory.
	I.	II.	III.	$C_{18}H_{12}O_3$.
C	77.81	77.99	78.09 per cent.	78.26 per cent.
H	5.07	5.00	4.51	4.35
O	17.12	17.01	17.40	17.39

This acid, therefore, has the formula $C_{18}H_{12}O_3$, and is produced from dehydrobenzoylacetic acid by the addition of two atoms of hydrogen and the elimination of the elements of water according to the equation—

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{12}O_3 + H_2O.$$

The yield of this acid is very small, and it appears to be formed only under certain conditions, the principal product of the reaction being the acid $C_{18}H_{14}O_4$, which will be described later on. In this reduction by far the greater part of the dehydrobenzoylacetic acid is entirely decomposed, a quantity of oily and resinous products being formed, which render the purification of the acids very difficult. It is curious that a considerable quantity of benzaldehyde always appears to be formed during the reduction. The acid $C_{18}H_{12}O_3$ melts at 112°. It is easily soluble in alcohol, benzene, ether, chloroform and bisulphide of carbon, almost insoluble in light petroleum. It is difficult to obtain it well crystallised, a mixture of benzene and light petroleum being the best solvents to crystallise it from. The bisulphide of carbon solution does not decolorise bromine.

The acid dissolves in concentrated sulphuric acid with an intense

orange coloration, which, on warming, first disappears and then turns to a greenish-brown.

Apparently, it is a very stable body, and is not affected by potassium permanganate in the cold, and only slowly on warming. Heated by itself in a test-tube it is decomposed into carbonic anhydride and high-boiling oils, a considerable quantity of carbonaceous matter being left behind. No acetophenone is formed when it is distilled with soda-lime.

The acid dissolves in soda and ammonia slowly in the cold, more rapidly on heating. The sodium salt is best prepared by dissolving the acid in a little alcohol, neutralising with soda, and allowing the solution to evaporate over sulphuric acid in a vacuum. Thus obtained it is an almost colorless syrup easily soluble in water; the solution, exposed for a long time over sulphuric acid in a vacuum, slowly deposits crystals. The quantity of this acid, $C_{18}H_{12}O_3$, which I obtained was unfortunately insufficient to allow of the further examination and analysis of its salts. The products of the reduction of dehydracetic acid were first examined by Oppenheim and Precht,[1] who, by treating this body with zinc and hydrochloric acid, obtained an acid melting at 187°; this, however, they did not further examine, only stating that it was not a simple reduction-product, but that it appeared to contain less oxygen than the dehydracetic acid. Schibbye,[2] who, during some experiments on dehydracetic acid, repeated this reaction, and analysed the acid and its barium salt, gave to the former the formula $C_8H_{10}O_3$, it being formed from dehydracetic acid according to the equation—

$$C_8H_8O_4 + 2H_2 = C_8H_{10}O_3 + H_2O.$$

If the reaction takes place in this way it is possible that the acid $C_{18}H_{12}O_3$, described above, is constituted similarly to the acid $C_8H_{10}O_3$, in which case the constitution of the former would have to be changed to $C_{18}H_{14}O_3$. I am at present engaged in some experiments to decide this point.

In order to isolate any other products of the reaction of dehydrobenzoylacetic acid, the mother-liquors from the acid $C_{18}H_{12}O_3$ were next evaporated to dryness, the semi-solid residue dissolved in a little alcohol, and light petroleum boiling at 70°–80° added until the liquid became slightly turbid. On allowing the solution to evaporate at the ordinary temperature, a new acid crystallised

[1] Berichte **9**, 1101. [2] Inaugural Dissertation, Würzburg, 1882.

out in small needles, which were collected, washed with alcohol and light petroleum, and dried at 110°. The analysis gave the following results:

I. 0.1568 gram substance gave 0.0731 gram H_2O and 0.4239 gram CO_2.

II. 0.1614 gram substance gave 0.0758 gram H_2O and 0.4364 gram CO_2.

III. 0.1511 gram substance gave 0.0705 gram H_2O and 0.4064 gram CO_2.

	Found.			Theory, $C_{18}H_{14}O_4$.
	I.	II.	III.	
C	73.73	73.74	73.36 per cent.	73.47 per cent.
H	5.18	5.22	5.18	4.76
O	21.09	21.04	21.46	21.76

The acid, therefore, has the formula $C_{18}H_{14}O_4$, and is formed from dehydrobenzoylacetic acid by the addition of two atoms of hydrogen, according to the equation—

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{14}O_4.$$

It crystallises from a mixture of alcohol and light petroleum in small yellow needles which melt at 145°–150° with decomposition and evolution of carbonic anhydride. It is easily soluble in most of the usual solvents, but only sparingly in light petroleum and cold bisulphide of carbon. From its hot solution in the latter it is deposited on cooling in nodules, seldom in well-formed crystals. The solution in bisulphide of carbon does not decolorise bromine at ordinary temperatures, but on warming hydrogen bromide is given off, and a brominated acid formed which crystallises out in small needles on cooling.

The acid $C_{18}H_{14}O_4$ is moderately soluble in dilute alkalis, especially on warming, and is reprecipitated on the addition of an acid. It dissolves in concentrated sulphuric acid, forming a yellow solution, which changes to brownish-red on warming. When heated in a test-tube it melts and gives off carbonic anhydride, a low-boiling oil distilling over with an odor like benzene; if the heating be continued the greater part chars, a small quantity of a heavy oil being formed which becomes solid on cooling, and appears to be benzoic acid. On distilling the acid with soda-lime a small amount of an oil of low boiling-point is formed, but no acetophenone.

Action of Acetic Anhydride on the Acid $C_{18}H_{14}O_4$.

From the formula of this acid it would seem to be the intermediate product in the formation of the acid $C_{18}H_{12}O_3$ by the reduction of dehydrobenzoylacetic acid, thus:

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{14}O_4 = C_{18}H_{12}O_3 + H_2O.$$

It appeared probable, therefore, that by treating it with some dehydrating agent, such as acetic anhydride, the acid $C_{18}H_{12}O_3$ would be produced. In order to test this two grams of the acid $C_{18}H_{14}O_4$ were heated with an excess of acetic anhydride in a flask connected with a reflux condenser for about one hour. Water was then added, and the precipitated product after washing with water was crystallised from 80 per cent. acetic acid. The analysis gave the following result:

I. 0.1910 gram substance gave 0.0817 gram H_2O and 0.5292 gram CO_2.

II. 0.2124 gram substance gave 0.0908 gram H_2O and 0.5871 gram CO_2.

	Found.		Theory. $C_{20}H_{14}O_4$.
	I.	II.	
C	75·57	75·39 per cent.	75·47 per cent.
H	4·75	4·75	4·40
O	19.68	19.86	20.13

This compound appears, therefore, to have the formula $C_{20}H_{14}O_4$, and it would seem as if the acetic anhydride had not only acted as a dehydrating agent, but that an acetate had also been formed, according to the equation—

$$C_{18}H_{14}O_4 + {}_2{}^{CH_3.CO}_{CH_3.CO}\!>\!O = C_{20}H_{14}O_4 + 3CH_3.COOH.$$

It is, however, impossible to come to any definite conclusion from this result, as the amount of material at my disposal was so small that I was unable to try this reaction again, and confirm the constitution of the compound $C_{20}H_{14}O_4$ by further analyses. It crystallises from acetic acid in yellow needles which melt at 145°–150°. Heated in a test-tube it first melts, and then gives off carbonic anhydride and acetic anhydride. From the ease with which it gives up its acetic anhydride it is possible that it is nothing more than a mixed anhydride of the acid $C_{18}H_{12}O_3$ and acetic acid. It is easily soluble in hot alcohol, less so in cold. It

dissolves easily in benzene and chloroform, but only sparingly in ether and bisulphide of carbon: in light petroleum it is almost insoluble. It is precipitated in small needles from its solution in benzene on adding light petroleum, and can be purified in this manner. It crystallises, however, best from dilute acetic acid (80 per cent.).

The alcoholic solution gives an intense scarlet coloration with ferric chloride. The compound is moderately soluble in ammonia, sodium hydroxide and carbonate, especially on warming. It dissolves in concentrated sulphuric acid, forming an orange solution, which changes to brown on heating. This coloration does not disappear on diluting with water.

Heated with alcoholic potash it is easily saponified, acetic acid and another acid being formed.

Action of Phosphorous Pentachloride on Dehydrobenzoylacetic Acid.

In order, if possible, to obtain some further clue as to the constitution of dehydrobenzoylacetic acid, it was next treated with phosphorous pentachloride. By this means, not only the carboxyl-group, but also any carbonyl- or hydroxyl-groups would be acted on and be replaced by chlorine, whereas any oxygen present in the indifferent or oxide form would remain intact, and could be easily recognised.

If dehydrobenzoylacetic acid is mixed with phosphorous pentachloride a very energetic reaction sets in, the whole becoming very hot and most of the acid being charred, so that it was found impossible to extract any crystalline compound from the product. It was necessary, therefore, to moderate the violence of the reaction by diluting with oxychloride of phosphorus and cooling, the experiment being carried out in the following way:

5 grams of dehydrobenzoylacetic acid were mixed with 30 grams of phosphorous oxychloride, and then 10 grams of phosphorous pentachloride were slowly added, the whole being kept thoroughly cooled with ice-water. The acid slowly dissolved in the mixture, forming a yellowish-brown solution, and on standing a quantity of yellow crystals were deposited, which, however, at a later stage of the reaction, disappeared again almost entirely. After remaining for twelve hours the product was poured into ice-water, when a yellowish semi-solid mass was precipitated; this was collected, well

washed with water, and dried over sulphuric acid in a vacuum. In about forty-eight hours the mass, which had become hard and brittle, was powdered and extracted with small quantities of hot alcohol, in which it was sparingly soluble, and filtered. The filtrate on cooling deposited a yellowish crystalline substance, which by one or two recrystallisations from methyl alcohol was obtained pure in colorless plates melting at 227°–229°.

The amount of this compound obtained by the above reaction was, however, so small that no analysis could be made. It appeared to contain only traces of chlorine. It is colored yellow on being warmed with potash.

The residue left after extracting the above-described substance with alcohol was dissolved in boiling methyl alcohol, from which it was deposited on cooling in beautiful brownish-colored glittering plates. On repeated recrystallisation from the same solvent it was easily obtained pure. For the analysis it was dried at 120° and then gave the following results:

I. 0.2114 gram substance gave 0.0691 gram H_2O and 0.5370 gram CO_2.

II. 0.2226 gram substance gave 0.0758 gram H_2O and 0.5668 gram CO_2.

III. 0.1394 gram substance gave 0.0665 gram AgCl.

IV. 0.2363 gram substance gave 0.1110 gram AgCl.

V. 0.2415 gram substance gave 0.1128 gram AgCl.

	Found.					Theory, $C_{18}H_{11}O_3Cl$.
	I.	II.	III.	IV.	V.	
C	69.28	69.44	...	...	...	69.56 per cent.
H	3.63	3.78	...	...	...	3.55
Cl	...	...	11.80	11.63	11.58	11.43

The compound, therefore, has the formula $C_{18}H_{11}O_3Cl$. When crystallised from methyl alcohol it forms brownish-colored plates melting at 150°–151°.

It is sparingly soluble in ether, alcohol, benzene and light petroleum, more easily in hot methyl alcohol and acetic acid. The hot alcoholic solution gives a reddish-brown coloration with ferric chloride. It dissolves with difficulty in sodium hydroxide, ammonia and sodium carbonate, forming yellow solutions, which, when acidified, deposit a colorless amorphous acid. On boiling with alcoholic potash for a short time, however, it is easily decomposed, and on evaporating the alcohol and adding water, a dark

brownish solution of a potassium salt is obtained; this, when acidified, deposits an oily acid, which was extracted with ether. On allowing the ethereal solution to evaporate a thick oily acid was obtained, and on standing a small quantity of a crystalline body was deposited; this, however, could not be obtained pure enough for analysis. The alcoholic solution of this acid gives an intense violet coloration with ferric chloride, very similar to that produced by benzoylacetic acid. As the formation of this latter acid appeared possible, the crude product of the above reaction was distilled, and a few drops of a brownish oil obtained, which smelt decidedly of acetophenone. The quantity was too small, however, to determine the boiling-point, and I was therefore unfortunately unable to decide definitely whether benzoylacetic acid had been formed or not. It appears, however, to be extremely probable. On simply warming the compound $C_{18}H_{11}O_3Cl$ with alcoholic potash it dissolves completely, and after a short time a potash salt crystallises out; this, when acidified, yields an acid which also gives the violet coloration with ferric chloride. On prolonged boiling with alcoholic potash, however, a neutral body is formed, and only a trace of the above acid. If a solution of this chloride in ether is treated with an ethereal solution of sodium ethoxide, a beautiful yellow sodium compound is precipitated. From these experiments it would seem that the compound $C_{18}H_{11}O_3Cl$ is in reality a chlorinated acid of the formula $C_{17}H_{10}OCl.COOH$, and not the acid chloride $C_{17}H_{11}O_2.COCl$, as might be expected from the mode of formation. In the latter case we should expect that dehydrobenzoylacetic acid would be regenerated on treating it with water; or on treating it with boiling alcohol or sodium ethoxide, that the ethylic salt of the latter would be formed, reactions which as a fact do not take place. I therefore propose to name the compound $C_{18}H_{11}O_3Cl$, "Chlorodehydrobenzoylacetic acid."

Heated by itself in small quantities at a time it first melts, and then at a high temperature a thick brown oil distils over, which on cooling slowly solidifies, a small quantity of a carbonaceous residue being left. The distillate after washing with a little alcohol melts at 147°–149°, and appears to be the unchanged substance, a proof that it is very stable. Chlorodehydrobenzoylacetic acid is easily reduced by warming it with zinc-dust and acetic acid. On adding water a pale yellowish substance is obtained, which is free

from chlorine. After collecting and washing with water the residue was dissolved in a little hot alcohol, from which it separated on cooling in amorphous flakes. On heating, this substance becomes brownish at about 130°, and melts at between 155°–160°; at a higher temperature carbonic anhydride is given off, and a blackish tarry residue is left. It dissolves in concentrated sulphuric acid with a beautiful purple color, but the solution soon becomes discolored on standing. It dissolves easily in benzene, and is precipitated in yellowish flakes on adding light petroleum, but as it could not be obtained in crystalline form from these or any other solvents, it was not analysed.

By the action of phosphorous pentachloride on dehydracetic acid, Oppenheim and Precht[1] obtained a compound of the formula $C_8H_6O_2Cl_2$, which is possibly the product of the further action of the above reagent on an unstable body $C_8H_7O_3Cl$, the latter being similarly constituted to chlorodehydrobenzoylacetic acid. In order to test this the action of an excess of phosphorous pentachloride on the compound $C_{18}H_{11}O_3Cl$ was tried, and, as a fact, traces of a second body were obtained, which, however, owing to the small quantity of material at my disposal, could not be further examined.

Constitution of Dehydrobenzoylacetic Acid.

Dehydrobenzoylacetic acid, $C_{18}H_{12}O_4$, contains besides a carboxyl-group COOH, and a carbonyl-group CO, a fourth atom of oxygen, which, on account of its indifference towards acetic anhydride, reducing agents and phosphorous pentachloride, can neither be present in the ketone form (CO) nor as hydroxyl, OH, and must therefore be in the ether form—*i. e.*, joined with its two affinities to two different carbon-atoms, thus: $\vdots C.O.C \vdots$. It is clear, moreover, that this acid contains two phenyl-groups, otherwise it could not be split up into two molecules of benzoylacetic acid on treatment with alcoholic potash.

In endeavoring from these facts to establish a formula for dehydrobenzoylacetic acid, it is first important to bear in mind that it is evidently formed by the elimination of two molecules of water from two molecules of benzoylacetic acid, thus:

$$\begin{matrix} C_6H_5.CO.CH_2.COOH \\ C_6H_5.CO.CH_2.COOH \end{matrix} = C_{18}H_{12}O_4 + 2H_2O.$$

[1] Berichte 9, 1100.

Dehydrobenzoylacetic acid is, however, a monobasic acid, forming salts of the formula $C_{18}H_{11}O_4M$, so that it follows that the carboxyl-group of one of the molecules of benzoylacetic acid must condense in some way with the second molecule of the latter, one molecule of water being eliminated. This intermediate product then loses a second molecule of water, dehydrobenzoylacetic acid being formed. The simplest way in which this condensation of two molecules of benzoylacetic acid can take place is the following:

$$\begin{array}{l} \mathrm{Ph.C(O)H_2C.COPh} \\ \mathrm{COOH.CH(HHO)OC^{\cdot}} \end{array} = \begin{array}{l} \mathrm{PhC:C.COPh} \\ \mathrm{COOH.CH:CO} \end{array} + 2H_2O.$$

That this formula is not the right one is evident, as it not only contains two ketone-groups, but is so strongly bound together that the splitting up into two molecules of benzoylacetic acid, on simply standing in contact with potash, would be extremely difficult to account for. Besides the above there are two other possible formulæ for dehydrobenzoylacetic acid, which can be built up on the assumption that the carboxyl-group of one molecule of benzoylacetic acid takes part in the reaction—namely:

I.
$$\begin{array}{l} \mathrm{COOH.C.CO.CH} \\ \quad\quad\| \quad\quad\| \\ \mathrm{PhC{-}O{-}CPh} \end{array}$$

II.
$$\begin{array}{l} \mathrm{Ph.C.O} \\ \quad\quad\| \\ \mathrm{COOH.C}\!-\!\!>\!\mathrm{C:CH.COPh.} \end{array}$$

In the formation of these two formulæ it is necessary to suppose that, as in almost all condensations of ethylic benzoylacetate and acetoacetate, the molecule first undergoes an internal change, thus

$$\underset{\text{Stable form.}}{\mathrm{C_6H_5.CO.CH_2.COOH}} = \underset{\text{Mobile form.}}{\mathrm{C_6H_5.C(OH):CH.COOH}}.$$

In formula I the condensation takes place between two such mobile forms, thus:

$$\begin{array}{l} \mathrm{COOH.C(HHO.)OC.CH} \\ \quad\quad\| \quad\quad\quad\quad\| \\ \mathrm{PhC.(OH\ H)O.CPh} \end{array} = \begin{array}{l} \mathrm{COOH.C.CO.CH} \\ \quad\quad\| \quad\quad\| \\ \mathrm{PhC{-}O{-}CPh} \end{array} + 2H_2O.$$

Formula II is formed in two stages. In the first place the carboxyl-group of one molecule of benzoylacetic acid (in the stable form) condenses with the second molecule (in the mobile form) in the following way:

$$\begin{array}{l} \mathrm{Ph.C.OH} \\ \| \\ \mathrm{COOH.C\boxed{H\ HO}OC.CH_2.COPh} \end{array} = \begin{array}{l} \mathrm{Ph.C.OH} \\ \| \\ \mathrm{COOH.C.CO.CH_2.COPh} \end{array} + \mathrm{H_2O}.$$

In the second part of the condensation this intermediate body must be transformed into the mobile form, which can take place in two ways. In the first place one of the hydrogen-atoms of the CH_2-group can react with the CO-group next to the phenyl-group, when the following mobile intermediate body would be formed:

$$\begin{array}{l} \mathrm{Ph.C.OH} \\ \| \\ \mathrm{COOH.C.CO.CH:C(OH)Ph}, \end{array}$$

which, on removing the elements of water from the two hydroxyl-groups, gives formula I.

In the second place the molecular change can take place between the CH_2-group and the other ketone-group, and thus give the following body:

$$\begin{array}{l} \mathrm{Ph.C.OH} \\ \| \\ \mathrm{COOH.C.C(OH):CH.COPh}, \end{array}$$

which, on the elimination of water, gives formula II, thus:

$$\begin{array}{l} \mathrm{Ph.C.O\boxed{H}} \\ \| \qquad\quad \lfloor \\ \mathrm{COOH.C.C\boxed{(OH)}:CH.COPh} \end{array} = \begin{array}{l} \mathrm{PhC.O} \\ \| \\ \mathrm{COOH.C-} \end{array} > \mathrm{C:CH.COPh} + \mathrm{H_2O}.$$

Of these two formulæ it is evident that, apart from the complicated formation of formula II, formula I is the most likely, as it explains best of all the reactions in which the acid takes part.

I therefore suggest as the most probable constitution of the dehydrobenzoylacetic acid the following formula:

$$\begin{array}{l} \mathrm{COOH.C.CO.CH} \\ \| \quad\ \| \\ \mathrm{C_6H_5.C-O-C.C_6H_5}. \end{array}$$

This body is split up on treatment with alcoholic potash into two molecules of benzoylacetic acid, thus:

$$\begin{array}{l} \mathrm{\quad H\ OH} \\ \mathrm{COOH.C.\ CO.CH} \\ \mathrm{\quad \|\ \ \ \|} \\ \mathrm{C_6H_5.C-O-C.C_6H_5} \\ \mathrm{\quad HO\ H} \end{array} = \begin{array}{l} \mathrm{COOH.CH} \\ \| \\ \mathrm{C_6H_5.C.OH} \end{array} + \begin{array}{l} \mathrm{COOH.CH} \\ \| \\ \mathrm{C_6H_5.C.OH} \end{array}.$$

The two acids, $C_{18}H_{14}O_4$ and $C_{18}H_{12}O_3$, produced by the action of nascent hydrogen on dehydrobenzoylacetic acid would therefore have the following formulæ:

$$\begin{matrix}\mathrm{COOH.C.CH(OH).CH}\\ \|\qquad\quad\|\\ \mathrm{Ph.C-O-CPh}\end{matrix}=C_{18}H_{14}O_4 \qquad \begin{matrix}\mathrm{COOH.C.CH:C}\\ \|\qquad\quad\|\\ \mathrm{Ph.C-O-CPh}\end{matrix}=C_{18}H_{12}O_3.$$

The formation of chlorodehydrobenzoylacetic acid by the action of pentachloride of phosphorus on dehydrobenzoylacetic acid undoubtedly takes place in two stages:

$$\text{I.}\quad \begin{matrix}\mathrm{COOH.C.CO.CH}\\ \|\qquad\quad\|\\ \mathrm{PhC-O-CPh}\end{matrix}+2PCl_5= \begin{matrix}\mathrm{COCl.C.CCl_2.CH}\\ \|\qquad\quad\|\\ \mathrm{PhC-O-C.Ph}\end{matrix}+2POCl_3+HCl;$$

$$\text{II.}\quad \begin{matrix}\mathrm{COCl.C.CCl_2.CH}\\ \|\qquad\quad\|\\ \mathrm{PhC-O-CPh}\end{matrix}+H_2O= \begin{matrix}\mathrm{COOH.C.CCl:C}\\ \|\qquad\quad\|\\ \mathrm{PhC-O-CPh}\end{matrix}+2HCl,$$

this reaction being in every way analogous to the formation of chlorocinnamic acid by the action of pentachloride of phosphorus on ethylic benzoylacetate as described in Part II[1] of this research.

On comparing the properties of dehydrobenzoylacetic acid with those of the dehydracetic acid it is evident that, although some minor differences do exist, these two compounds are most probably of an analogous constitution; and as the former is extremely difficult to get in any quantity, I have commenced working on the latter, and hope at some future time to make public the results of my experiments.

ON A SOURCE OF ERROR IN THE ESTIMATION OF UREA BY THE HYPOBROMITE METHOD, WITH APPARATUS OF THE RUSSELL AND WEST TYPE.

By Walter D. Green.

Of the many forms of apparatus employed for estimating the amount of urea contained in urine by means of akaline hypobro-

[1] This Journal **7**, 153.

mite or hypochlorite solutions, probably the one most used by physicians is that devised by Russell and West. These experimenters, by using an alkaline solution of sodium hypobromite, and measuring the nitrogen evolved from the decomposition of the urea in urine, found that with their apparatus 94 or 95 per cent. of the urea present could be estimated. The reaction may be expressed as follows:

$$(NH_2)_2CO + 3NaBrO = 2H_2O + CO_2 + 3NaBr + N_2.$$

According to Knop,[1] the solution of sodium hypobromite should be prepared as follows: Dissolve 100 grams of sodium hydroxide in 250 cc. of water. Allow this solution to cool, and then add 25 cc. of bromine. Upon cooling, the reagent is ready for use. Thus prepared, the solution contains 62.5 grams free sodium hydroxide. Hitherto it has been thought that all the carbon dioxide evolved during the decomposition of the urea was absorbed by the free sodium hydroxide in the hypobromite solution to form sodium carbonate, and in employing this method with the Russell and West apparatus, the percentage of urea has been found to be equal to that originally present in the urea solution employed, and sometimes rather in excess of the amount really present. This was suspected to be due to the non-absorption of an appreciable quantity of the carbon dioxide evolved during the decomposition of the urea. In order to determine this, the following described apparatus was devised and the accompanying experiments performed; the object being to ascertain if any carbon dioxide was collected unabsorbed with the nitrogen and was measured as nitrogen, and if so, to what extent this took place. The apparatus consisted of a wide-necked bottle containing a small test-tube, in which the decomposition of the urea was to take place, closely stoppered with a rubber cork through which two glass tubes pass, one of which can be pushed down to within an inch of the bottom of the bottle. Connected with this tube upon one side of the bottle was a drying apparatus, consisting of five cylinders, containing respectively a solution of calcium hydrate, caustic soda in sticks, barium hydrate solution, and caustic soda in sticks. The air being admitted to the first cylinder, passes successively through them and is deprived of its carbon dioxide. A pinch-cock prevents any gas during its evolution in the bottle from passing into

[1] Chem. Centralbl. 1860, 244.

the cylinders. Attached to the remaining tube emerging from the bottle was a drying-tube containing calcium chloride in small pieces. Next were the Geissler's bulbs for collecting the carbon dioxide escaping absorption in the bottle. These were followed by another calcium chloride drying-tube to prevent access of any moisture from the atmosphere. A rubber tube attached to this drying-tube and connected with an aspirator, rendered it possible to exhaust the apparatus.

To detect qualitatively the presence of carbon dioxide with the nitrogen, a U-tube containing a strong solution of barium hydrate was inserted in place of the Geissler's bulbs. The urea solution was placed in a small test-tube, and introduced into the bottle into which 30 cc. of the hypobromite solution had been poured, and the pinch-cock between it and the drying-cylinders closed. Then upon inclining the bottle containing the reagent with the urea solution in the test-tube, immediate decomposition ensued with the evolution of gas. Ten minutes after the completion of the decomposition in the bottle, the first described tube passing through the cork was pushed down to within half an inch of the surface of the liquid in the bottle, and the pinch-cocks having been opened, aspiration was begun, and air free from carbon dioxide was slowly drawn through the apparatus for about half an hour.

The presence of carbon dioxide was demonstrated several times without doubt by the turbidity of the barium hydrate solution in the U-tube, upon drawing pure air through the bottle in which the decomposition occurred. To determine the actual amount of carbon dioxide passing over with the nitrogen, a weighed set of Geissler's bulbs, containing a strong solution of potassium hydrate, was placed in the position previously occupied by the U-tube after the calcium chloride tube, and connected as before. The method of procedure as to aspiration, etc., was the same as previously described. The bulbs were weighed both before each experiment and at its close, being at these times and as soon as detached from the apparatus tightly corked with rubber, so as to exclude admission of carbon dioxide and moisture from the air. The increase in weight after the passage of the gas is equal to the amount of carbon dioxide absorbed, which in the use of the Russell and West apparatus and of apparatus of that general design is measured as nitrogen. The accompanying table shows the results of fourteen quantitative experiments made with varying quantities of a 5 per cent. urea solution :

No. of Experiment.	No. cc. urea used.	Increase in weight of Geissler bulbs.	Equivalent volume of CO_2 in cc.
1	1	0.001	0.508
2	1	0.0003	0.152
3	1	0.0003	0.152
4	1	0.0007	0.355
5	2	0.001	0.507
6	1	0.0002	0.1015
7	2	0.0011	0.558
8	2	0.0017	0.862
9	2	0.0007	0.355
10	3	0.0004	0.202
11	3	0.0026	1.318
12	3	0.0011	0.558
13	4	0.0012	0.608
14	4	0.0049	2.485

Upon examination of the foregoing results it will be observed that an appreciable quantity of carbon dioxide escapes absorption by the free sodium hydrate contained in the sodium hypobromite solution, and passing out along with the nitrogen, is measured as such, thus increasing the apparent amount of urea in the solution undergoing analysis. The objection to the employment of the Russell and West type of apparatus is this non-absorption of all the carbon dioxide, which is most likely due to the immediate decomposition of the urea coming into contact with *only the surface* of the hypobromite solution in the bottle. This decomposition takes place so rapidly that sufficient time is not allowed for absorption of the carbon dioxide by the caustic soda, and possibly too the caustic soda in the immediate vicinity of the place of decomposition becomes saturated with carbon dioxide.

In the apparatus of Hüfner,[1] and that lately devised by Dr. Wm. H. Greene,[2] in which the evolved gases are obliged to pass through a long column of the sodium hyprobromite solution, the conditions exist for the complete absorption of the carbon dioxide with the least possible likelihood of error. But, even in employing these apparatus, the theoretical quantity of nitrogen (372 cc. from 1.0 gram of urea) is not obtained, but according to Hüfner only 354.33 cc. at 0° C. and 760 mm. pressure.

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[1] Zeitschr. f. physiol. Chem. **1**, 350. [2] Comptes Rendus **97**, 1141.

A CONTRIBUTION TO THE KNOWLEDGE OF THE ACTION OF CACODYLIC ACID ON THE ANIMAL ECONOMY.

By John Marshall and Walter D. Green.

The only arsenic compounds in which the toxic properties of the arsenic is doubtful are the so-called arsenic-methyl bodies or cacodyl compounds. In the literature of the subject much conflicting testimony exists relative to the poisonous properties of these compounds, and especially concerning one of them, cacodylic acid, which has been selected as the subject of investigation in this paper. Cacodylic acid, $(CH_3)_2AsOOH$, contains 54.35 per cent. of metallic arsenic equal to 71.4 per cent. of arsenious oxide.

According to Bunsen,[1] who in 1843 was one of the first to investigate the action of this substance upon the animal economy, it has been taken in large doses, and is not in the slightest degree poisonous. Prof. Kürschner[2] (quoted by Bunsen) in his researches proved the fact without doubt, and Bunsen's earlier observations upon frogs were fully confirmed. Bunsen[3] injected six grains of cacodylic acid, presumably by means of a syringe with a long tube attached, into the stomach of a rabbit without the evidence of even the slightest distress on the part of the animal. Seven grains of the acid were injected into the jugular vein of a rabbit without injurious effect. Four grains of the acid were, in a manner not described, injected into the lungs of a rabbit and no symptoms of poisoning were developed. Bunsen concluded from these results that, on account of the manner of combination of the arsenic in cacodylic acid, it is deprived of its poisonous properties.

Bunsen[4] injected eight grams (evidently should be grains) of the acid dissolved in water into the jugular vein of a rabbit without producing any unfavorable symptoms.

Schmidt and Chomse[5] made three experiments upon animals with *perfectly pure cacodylic acid*, and found it to possess no poisonous properties. Their first experiment was performed upon

[1] Annalen der Chemie **46**, 10. [2] Pogg. Ann. **42**, 140. [3] *Ibid.*
[4] Annales de Chimie et Phys., 3 Serie, **8**, 358.
[5] Moleschott's Unters. z. Naturlehre **6**, 122; 1860.

a young cat which had not been fed for twenty-four hours. One gram of cacodylic acid was administered in bread-pills. In thirty minutes the animal showed signs of distress and began to vomit, in which vomit nearly all the pills given were ejected. Very little of the pills was dissolved, as the outside only was softened. Fifteen minutes afterwards the vomiting again commenced, and occurred three times in the following forty-five minutes. During the whole time the cat seemed to be quite lively, and only towards the last, on account of the oft-repeated vomiting, did she show signs of distress.

2. One gram of cacodylic acid dissolved in water was introduced into the stomach of a young cat which had been well fed for twelve hours previously. One and three-quarter hours afterwards vomiting began, which continued for fifteen minutes. Soon afterward liquid feces were ejected, and occurred again two and a quarter hours later. During the whole period the cat showed no other symptoms of distress. She afterward ate with great relish.

3. A mare of torpid constitution, but otherwise physiologically normal (pulse 36, respiration 9), was treated with one gram of cacodylic acid in solution thrown into the left jugular vein. Soon after the injection there was an increase in the pulse, which in the fourth hour settled down to 32. Five hours after the injection nothing other than the previous normal condition of the animal was observed, save that the pulse was 32. In every case cacodylic acid was found by them, in the feces and urine, by reducing the acid to cacodylic oxide with phosphorous acid. Schmidt and Chomse concluded from the result of these experiments that cacodylic acid possessed no poisonous properties.

Lebahn,[1] however, who performed a series of experiments under the direction of Prof. Schulze, Sr., declares from the results of his experiments that cacodylic acid does possess poisonous properties, and that its toxic symptoms are like those of ordinary arsenical poisoning. He experimented wholly upon rabbits, and found that all those (10) to whom the acid was administered died.

Lebahn's Experiments.

1. After the administration of 0.071 gram of cacodylic acid, in four separate portions, into the jugular vein, also dissolved in milk and injected under the skin, the animal died in sixteen days.

[1] Ein Beitrag zur Kenntniss der Wirkung der Kakodylsäure. Dissert., Rostock, 1868.

2. 0.022 gram of the acid given in three portions: twice in milk and once injected under the skin. The animal died in eight days.

3. 0.083 gram of the acid injected under the skin at one time. The animal died in twenty days.

4. 0.166 gram injected under the skin. Animal died in twenty-five days.

5. 0.25 gram injected under the skin. The animal died in eighteen days.

6. 0.2 gram of arsenious oxide injected into the mouth by means of a syringe in two separate portions. Animal died in sixty hours.

7. 0.5 gram of cacodylic acid injected into the mouth. Animal died in ninety-four hours.

8. 0.5 gram of the acid injected into the mouth. Animal died in twenty-three hours.

9. 0.75 gram of the acid injected into the mouth. Animal died in twenty-nine hours.

10. 2.3 grams of the acid, in three portions, injected into the mouth. Animal died in eight days.

Lebahn also found cacodylic acid, as described by Schmidt and Chomse, in the urine and feces by reducing to cacodylic oxide with phosphorous acid.

A quantity of crystalline acid was obtained from a Philadelphia manufacturer of fine chemicals, and the following experiments were performed with one cat and three rabbits:

1.—Sept. 24, 1885. To a young male cat of about 1500 grams weight was administered, at 1.08 P. M., 0.5 gram of cacodylic acid dissolved in about 5 cc. of water. The following effects were produced:

1.45 P. M. Violent retching.
2.35 P. M. Cat vomited. Very sick.
2.40 P. M. Vomited a curdy white material.
2.44 P. M. Vomited a curdy white material.
2.48 P. M. Copious soft, greenish defecation.
2.50 P. M. Marked salivation appeared.
2.52 P. M. Vomited.
2.57 P. M. Vomited and refused to drink water.
3.00 P. M. Copious urination occurred. Cat very restless and in pain. Moaning.

3.10 P. M. Vomited frothy white material. The garlic-like odor due to cacodyl compounds was strongly apparent upon the breath.

The following day (Sept. 25) 0.3 gram of cacodylic acid was given hypodermically to the same cat. Very profuse salivation was immediately noticed. Neither cacodylic acid nor arsenic could be detected in the saliva. The garlic-like odor was again noticed upon the breath. At this juncture the cat escaped, but was recovered two days afterwards in good health.

2.—Sept. 24, 1885. A female rabbit. Weight, about 2500 grams. At 1.30 P. M. 0.1 gram of the acid was administered hypodermically. The animal became very restless. On the following day, Sept. 25, a copious urination occurred at 11.25 A. M. The urine contained jelly-like masses, which under the microscope were found to be mucus. The animal ate food with seeming relish.

3.00 P. M. Urine drawn with a catheter. The presence of cacodylic acid was distinctly determined in it.

3.30 P. M. 0.5 gram of the acid was injected hypodermically. Garlic-like odor was noticed upon the breath. The administration of the acid was stopped. There were no ill effects, except a very noticeable restlessness. The animal entirely recovered.

3.—Sept. 28, 1885. Female rabbit. Weight, 1800 grams.

3.30 P. M. 0.5 gram of the acid was given by the mouth.

4.00 P. M. Salivation noticed. The animal became very sick. No more acid was administered, and the animal fully recovered.

4.—Sept. 29, 1885. Male rabbit. Weight, 1630 grams.

1.00 P. M. Was given 0.5 gram of the acid in solution by the mouth.

1.30 P. M. Animal very restless. Shaking head violently from side to side.

Sept. 30, 1885. Animal ate food readily.

11.25 A. M. Copious discharge of urine, containing jelly-like masses, which proved to be mucus.

1.00 P. M. 0.5 gram of the acid in solution was given by the mouth. Garlic-like odor was very strong on the breath. The animal died during the night.

Post-mortem. Oct. 1, ten hours after death. Stomach full of partly digested grass. Bladder half full of urine. Large intestine greatly distended with liquid colored yellow by feces. The whole alimentary tract showed evidences of a severe gastro-enteritis. Cacodylic acid could not be detected in the brain, but was found

in the kidneys. Phosphorous acid was employed to detect the presence of the acid.

It was observed at this juncture that the cacodylic acid that was employed was not entirely soluble in water, a slight residue always remaining undissolved. Upon examining this insoluble residue microscopically, it was found to be composed of perfectly formed octahedral crystals, which on further testing proved to be arsenious oxide. The remainder of the acid was treated with alcohol, which dissolved the larger part of it. The undissolved portion consisted of octahedral crystals of arsenious oxide. The alcoholic solution was filtered, and the filtrate allowed to evaporate at a low temperature. The resulting crystals were again treated with alcohol, and an insoluble residue of crystalline arsenious oxide was again observed. This recrystallisation after filtration was repeated several times, and each time an insoluble residue of arsenious oxide remained. The fact of this contamination of the cacodylic acid with arsenious oxide necessarily vitiates the results obtained in the preceding experiments.

As Lebahn,[1] in his paper, does not refer to the purity of the cacodylic acid employed by him, it may be possible that the acid he used was contaminated with arsenious oxide, and that the death of the animals used in his observations was not produced by cacodylic acid, but by arsenious oxide.

A new series of experiments was now begun with cacodylic acid obtained from Kahlbaum, of Berlin. It was first, however, thoroughly examined concerning its purity.

1. The crystals were colorless and odorless. Easily soluble in alcohol.

2. An aqueous solution reddened blue litmus.

3. Hydrogen sulphide produced in a water solution a white milkiness, which did not disappear upon boiling.

4. Warmed with phosphorous acid a strong odor of cacodyl was produced, and at the same time the evolution of thick, white fumes of cacodyl oxide was observed.

5. The acid in water solution with mercuric chloride gave a white crystalline precipitate of needle-like crystals, which on heating to boiling did not disappear.

6. A water solution of the acid boiled with red mercuric oxide

[1] *Loc. cit.*

caused no change—*i. e.*, no reduction of mercuric oxide. The filtrate upon cooling was clear, and was not tinged by hydrogen sulphide.

7. The solution of the acid with stannous chloride produced a strong, white cloudiness, and upon warming, a very penetrating odor of cacodyl chloride.

8. Silver nitrate added to a water solution of the acid produced a white precipitate, which on heating turned brown. The liquid had no odor. The precipitate increased upon the addition of ammonium hydroxide, but dissolved in excess of the latter reagent with the production of a brown coloration. Upon boiling this ammoniacal solution a silver mirror was formed, and the liquid became clear and colorless.

9. A water solution of the acid, placed with hydrochloric acid and zinc in a gas-evolution apparatus whose exit-tube led into a solution of silver nitrate, produced a brown, flocculent precipitate in the latter solution, and at the same time, heavy, white fumes were produced in the flask.

10. Barium and calcium hydroxides, calcium chloride and plumbic acetate produced no change in a water solution of the acid.

11. Zinc and platinum in galvanic circuit quickly produced the odor of cacodyl in a water solution of the acid.

It may be taken as conclusive, from the reactions above described, and the physical properties of the crystals employed, that the material was perfectly pure cacodylic acid.

Experiments with Kahlbaum's Cacodylic Acid.

1.—October 10, 1885. A female dog. Weight, 12 kilos.

At 10.35 A. M. 0.5 gram of the acid dissolved in 5 cc. of water was given by the mouth.

10.47 A. M. Vomited. Greatly distressed.

11.05 A. M. 0.5 gram dissolved in 5 cc. of water was given by the mouth. Dog very uneasy. Moaned with pain.

11.27 A. M. Defecated with great pain. Large, dark, loose feces.

12.25 A. M. Vomited curdy white material.

1.15 P. M. 0.1 gram of acid dissolved in 5 cc. of water was given by the mouth. The dog escaped at this juncture, but was recovered three days later in a healthy condition.

November 7, 1885. The dog was kept until this time (twenty-eight days), no more cacodylic acid having been administered since

the amount of 0.1 gram given October 10. The animal was killed, and an autopsy made, which showed an evident gastro-enteritis, and also congestion of the liver, lungs and peritoneum.

2.—October 15, 1885. Dog. Weight, 18 kilos. Dog had not been fed for thirty-six hours.

At 10.30 A. M. 0.2 gram of the acid dissolved in 5 cc. of water was given by the mouth.

10.35 A. M. Salivation produced.

10.50 A. M. Vomited green, frothy matter. Breath had garlic-like odor of cacodyl. Dog lively.

11.30 A. M. 0.1 gram dissolved in 5 cc. of water given by mouth. Garlic odor on breath. Dog lively.

12.30 P. M. 0.1 gram administered as above.

1.30 P. M. 0.1 gram administered as above.

2.30 P. M. 0.1 gram administered as above.

3.30 P. M. 0.3 gram administered as above.

4.25 P. M. Dog vomited, and at same time defecated. Feces soft and yellowish, with a strong garlic-like odor. Dog very sick.

4.30 P. M. 0.2 gram administered by mouth. Dog sick.

4.35 P. M. Vomited.

5.30 P. M. 0.1 gram given by mouth. Breath still has garlic-like odor. Dog very sick.

October 16, 1885. Same dog. Fed at 8.30 A. M. Dog lively. Breath still has garlic odor.

11.00 A. M. 0.2 gram dissolved in 5 cc. of water given by mouth.

11.45 A. M. Vomited.

2.00 P. M. 0.1 gram administered by mouth. Garlic odor.

3.00 P. M. 0.1 gram administered by mouth. Garlic odor.

4.00 P. M. 0.1 gram administered by mouth. Garlic odor.

5.00 P. M. 0.1 gram administered by mouth. Garlic odor.

6.00 P. M. 0.1 gram administered by mouth. Garlic odor. Dog defecated during the night. Feces were bloody and mucous-like, with garlic-like odor.

October 17, 1885. Same dog. Fed at 8.30 A. M. Lively in spirits.

11.30 A. M. 0.1 gram dissolved in 5 cc. of water given by mouth.

11.50 A. M. Salivation appeared.

12.00 M. Pulse 103; respiration 17. Defecated light yellow mucous-like feces with a strong garlic odor.

12.30 P. M. 0.1 gram was given in a small piece of meat.

1.30 P. M. 0.1 gram was given in a small piece of meat.

2.30 P. M. 0.1 gram was given in a small piece of meat. Ate a large piece of meat. Dog shows no evidence of distress.

3.30 P. M. 0.1 gram was given in a small piece of meat.

4.30 P. M. 0.1 gram was given in a small piece of meat.

5.30 P. M. 0.1 gram was given in a small piece of meat. Defecated three times during the night. The feces were soft, slimy, mucous-like and streaked with blood.

October 18, 1885. Same dog. Dog lively.

11.00 A. M. 0.2 gram administered in a small piece of meat.

11.35 A. M. Vomited.

12.00 M. 0.2 gram administered in small piece of meat.

1.00 P. M. 0.1 gram administered in small piece of meat.

2.00 P. M. 0.1 gram administered in small piece of meat.

October 22, 1885. Same dog. Condition unchanged. At 1.00 P. M. 3.0 grams of the acid dissolved in 10 cc. of water were injected into the jugular vein.

1.10 P. M. Vomited.

1.15 P. M. Vomited green, slimy material, which when tested was found to contain cacodylic acid. There were no solids in the vomit. Dog had two large liquid defecations.

October 23, 1885. Dog lively. Eyes congested. Long strings of mucus depended from eyelids. Conjunctiva greatly inflamed.

October 31, 1885. Same dog. Condition good. At 1.30 P. M. 2.0 grams of the acid dissolved in 10 cc. of water were injected into the jugular vein.

1.35 P. M. Animal distressed.

1.42 P. M. Vomited slimy, greenish matter, which did not contain cacodylic acid.

1.55 P. M. Vomited slightly. Same material as before. Cacodylic acid was found in this vomit.

2.00 P. M. Animal greatly distressed.

3.00 P. M. 7.0 grams dissolved in 30 cc. of water injected in the jugular vein. No untoward effects were noticed, and fifteen minutes later the dog was killed by severing the spinal cord. Throughout the whole experiment (seven days) the dog's urine was examined for cacodylic acid, which was found in every case. The feces of October 16, 17 and 18, treated separately with distilled water, warmed, filtered, and the filtrate evaporated to dryness at a

low temperature, showed the presence of cacodylic acid by giving off a strong cacodylic odor when warmed with phosphorous acid.

Results of Autopsy.—Intense inflammation of the stomach, intestines and lungs. Peritoneum injected. The mucous membranes covered with a thick pus. Intensely congested. Spleen enlarged. Kidneys congested.

Microscopic Examination of the Organs.

Lungs.—The blood-vessel walls were thickened, and their lumen everywhere filled with blood. The small capillaries and veins everywhere congested. Lung tissue generally inflamed. The alveolar walls were thickened by cell infiltration, and many of the air vesicles showed distinct catarrhal change, some being filled with epithelial cells, others with a lymphoid exudation, and still others were infarcted with blood. The appearance of the organs generally was that caused by an acute catarrhal pneumonia. In some of the more intensely inflamed portions there was observed numerous yellow, needle-like and cone-shaped crystals resembling hippuric acid. *Spleen.*—Appeared pigmented, which was probably due to the coloring matter of the blood, either in the shape of hæmin crystals or of an amorphous precipitate. The blood-vessels were all intensely congested, and the trabeculæ of the smooth, muscular tissue appeared unusually thick; otherwise nothing abnormal was observed. *Liver and Stomach.*—Showed cloudy swelling of the cells, due to inflammation. *Kidneys.*—Showed same cloudy swelling and a slight degeneration of the epithelium. Heart muscle did not show any morphological changes, and the blood generally was unaltered.

3.—November 3, 1885. Dog of about 15 kilos. weight.

1.50 P. M. 2.0 grams of the acid dissolved in 15 cc. of water were injected into the jugular vein.

1.55 P. M. Dog distressed.

1.56 P. M. Vomited green, slimy material.

1.58 P. M. Vomited same matter again.

2.00 P. M. Defecated. Feces loose and yellowish.

2.02 P. M. Vomited green, slimy material. A very small amount of cacodylic acid was found in this vomit.

2.10 P. M. Distress disappearing. Dog did not die. He was kept in view for several weeks afterward.

4.—November 14, 1885. Dog of 10 kilos. weight.

12.00 M. 3.0 grams of acid dissolved in 20 cc. of water were injected into the jugular vein.

12.10 P. M. Profuse salivation. Respirations, 180 per minute. Dog very sick. Lies down and is unable to get up.

12.35 P. M. Respirations much slower. Dog very uneasy.

12.38 P. M. Attempts to stand, but falls.

12.40 P. M. Gets up and drinks. Staggering gait. Weakness of whole right side manifest.

November 15, 1885. 10.00 A. M. Dog vomited twice during the night. Both ejections contained cacodylic acid. Dog lively and ate with evident relish. This dog lived several weeks, and was subsequently used for other purposes.

5.—November 7, 1885. Small dog weighing about 5 kilos.

2.00 P. M. 3.0 grams of the acid dissolved in 20 cc. of water were injected into the jugular veins.

2.04 P. M. Vomited a small quantity of slimy, greenish matter. No cacodylic acid was found in this vomit.

2.10 P. M. Extreme salivation. Great pain.

3.10 P. M. Staggering gait. Dog leans to the right side. Tactile sensibility lost. Pupils dilated evenly. Respirations slow and labored. Dog moans as if in pain.

3.40 P. M. Dog rises with much difficulty and immediately falls.

4.45 P. M. Dog died.

The evident cause of death in this experiment was the enormous amount of the acid in proportion to the weight of the dog, which was introduced directly into the circulation. Immediately after injecting the acid the blood-pressure tracings were taken with the kymographion, showing slowing of pulse and decrease in arterial pressure.

Autopsy.—Peritoneum greatly injected. Intestines congested and mucous membrane covered with pus. Lungs congested. Left auricle full of dark, unclotted blood. Urine evaporated to dryness and tested showed presence of cacodylic acid strongly.

According to Schmidt and Stürzwag,[1] upon the administration of arsenious oxide nervous symptoms occur, due to spinal irritation and paralysis. To the spinal irritation may be ascribed the vomiting and slowing of respiration, and also the partial paralysis or convulsive movements. These same symptoms occurred in the foregoing experiments with cacodylic acid, except the paralysis

[1] Moleschott's Unters. z. Naturlehr. **6**, 296.

and convulsive movements, which only existed in a slight degree. Schmidt and Stürzwag observed a decided weakness in the hind extremities, so that the animal was unable to stand. The same was observed in the preceding experiments with the acid. Schmidt and Stürzwag also noticed that a peculiar condition of somnolence occurred, in which movements were uncertain. This was also noticed in these experiments with cacodylic acid. The weakness, however, in all cases experimented upon with the acid was unilateral, resembling hemiplegia. In Schmidt and Stürzwag's cases diarrhœa was observed in nearly all the animals. This was noticed in all the experiments in the present investigation.

Lebahn observed that the action of cacodylic acid and arsenious oxide produce nearly analogous symptoms, and that the pathological changes were the same. The foregoing experiments confirm Lebahn's observations as far as the symptoms are concerned (*i. e.*, the analogous symptoms produced by cacodylic acid and arsenious oxide); but, as has been shown by the experiments described in this paper, cacodylic acid is not fatal in its effects. The fatal terminations in Lebahn's cases were probably due to an impure acid which he may have employed, which, as has been shown in the first part of this paper, may very readily happen. Lebahn concluded from his results that a part of the cacodylic acid was, by the action of the blood, decomposed, and that the arsenic set free entered into combination in its inorganic form with an alkali, and in this manner acted upon the organism. A part of the cacodylic acid may be given off by the lungs as paracacodylic oxide (*vide* the garlic-like odor on breaths), and the rest of it is excreted by means of the urine and feces as cacodylic acid. The formation of paracacodylic oxide may be the cause of the vomiting. Schmidt and Chomse[1] found that by the injection of the acid into the blood no perceptible action was produced. In the experiments described in this paper it may be observed that the action of the acid (causing vomiting, purging, etc.) was the same, whether given by the mouth or injected directly into the circulation. Finally, then, judging from the results of the experiments herein described, it may be concluded that cacodylic acid is not a poisonous substance in the general acceptation of the word poison.

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[1] *Loc. cit.*

ON THE VALUE OF BRÜCKE'S METHOD FOR THE REMOVAL OF INTERFERING SUBSTANCES FROM URINE IN TESTING FOR GLUCOSE.

By Edgar Moore Green.

In determining the presence of glucose in diabetic urine by any of the copper tests it is found that, under certain circumstances, some of the normal constituents of urine, such as creatinine and uric acid, interfere with the reaction of these tests. In the ordinary course of a case of diabetes, when the urine contains an abundance of glucose, usually no difficulty is experienced in obtaining the reactions; but after the patient has been restricted to a diet of nitrogenous food alone, great difficulty is often found in making the tests, because of a diminution in the amount of glucose and an increase in the amount of the interfering substances, creatinine, uric acid, etc. It may therefore be necessary to remove these substances before testing for the glucose. The method for their removal suggested by Brücke, and in use many years, consisted in adding neutral plumbic acetate, $Pb(C_2H_3O_2)_2$, to the urine, and immediately afterward adding plumbic tribasic acetate, $Pb_3O_2(C_2H_3O_2)_2$. The precipitate was then separated by filtration and washed with distilled water. The filtrate and washings having been collected in one vessel, ammonium hydroxide was added, which threw down the glucose in combination with the lead in the form of lead saccharate, $(PbO)_3(C_6H_{12}O_6)_2$. This white precipitate was collected on a filter-paper, washed, and then suspended in distilled water, and hydrogen sulphide, which decomposed the compound, passed through it. The filtered solution contained the glucose;[1] and it was used for the tests, after the hydrogen sulphide had been driven off by evaporation.[2] The original paper by Brücke could not be obtained, as it was not to be found in the journal referred to by Neubauer and Vogel. However, Beale gives the same method as the preceding. According

[1] The neutral plumbic acetate removes the sulphates, phosphates, and carbonates. The plumbic tribasic acetate precipitates the coloring matter, and at least a portion of the uric acid and creatinine. Probably a small amount of uric acid is contained in the precipitate of lead saccharate, and the remainder of the uric acid and creatinine, together with the urea, are contained in the filtrate after removal of the lead saccharate.

[2] Neubauer and Vogel. 8th Ed., 1881, 165.

to Bence Jones, "the seventh of a grain of glucose may be detected, when diluted with upwards of six ounces of water, and two-thirds of the total quantity of glucose present in a solution can be separated by this process."[1]

The method of Brücke, as given by Salkowski and Leube,[2] is as follows: Neutral plumbic acetate is first added to the urine, which is then filtered. Plumbic tribasic acetate and, afterward, ammonium hydroxide are added to the filtrate. After collecting the precipitate on a filter it is washed and suspended in water, hydrogen sulphide passed through it, and the evaporated solution employed for making the tests for glucose.

Although certain statements have been made by different writers as to the amount of glucose recovered after the use of this process, yet, so far as could be learned, no accurate experiments had been made to verify these statements. For this reason the experiments here described were undertaken for the estimation of this amount, and the determination thereby, if possible, of the practical value of the process. For it is readily seen that if a large percentage of the glucose is lost in the procedure, when but a relatively small amount had been present, that which remains may not be sufficient to give the proper reactions. Hence it might be thought that no glucose is present, when it has really been present in the original urine. In making the experiments, fresh normal urine, free from glucose, was used, and to certain quantities of this were added definite amounts of pure crystallised glucose. The first method attempted was the following: Three portions of urine containing definite amounts of glucose were employed: 100 cc. of urine containing 1.0 gram of glucose; 100 cc. of urine containing 0.5 gram of glucose; 100 cc. of urine containing 0.1 gram of glucose. Each of these quantities of urine, after the glucose had been thoroughly dissolved, was then divided into two parts of 50 cc. each, and the two samples worked at the same time. To each of these portions of urine were added 35 cc. of a 10 per cent. solution of neutral plumbic acetate. It was then stirred and filtered, and the precipitate washed with water in six portions of 5 cc. each. The filtrate and wash-water were collected together and stood aside. (For convenience this will be designated filtrate *A*.) The precipitate was suspended in about 50 cc. of water, warmed, and hydrogen sulphide passed through it until all the lead was pre-

[1] Beale, "Kidney Diseases, Urinary Deposits and Calculous Disorders." 3d Ed., 249.
[2] "Die Lehre vom Harn." 1882, 224.

cipitated, and then filtered. The precipitate was then washed with water in five portions of 5 cc. each, and the filtrate and wash-water evaporated to dryness on a water-bath. The dry residue was extracted with three or more portions of 5 or 8 cc. each of alcohol (to get rid of uric acid). The solution was filtered through a small filter, and the residue washed with about 15 cc. of alcohol. The alcoholic extract with the washings was evaporated to dryness on a water-bath.[1] The dry residue was dissolved in water, the volume of the solution carefully ascertained, and the amount of glucose present determined by means of Fehling's solution or the saccharimeter.

To filtrate *A*, obtained after the addition of neutral plumbic acetate to the urine, were added 15 cc. of plumbic tribasic acetate.[2] After being stirred and filtered, the precipitate was washed with water in six portions of 5 cc. each. (The filtrate and wash-water will be designated *B*.) The precipitate was suspended in about 50 cc. of water, warmed, and hydrogen sulphide passed through it until all the lead was precipitated. It was then filtered, and the precipitate washed with water in five portions of 5 cc. each. The filtrate and wash-water, collected together, were evaporated to dryness on a water-bath, the residue extracted with methyl alcohol, filtered, washed with more alcohol, and evaporated to dryness on a water-bath. The dry residue remaining was extracted with water, the volume of the solution ascertained, and the amount of glucose present determined as in the previous instance.

To filtrate *B* with wash-water, obtained after the precipitation by plumbic tribasic acetate, was added ammonium hydroxide until the solution had a slight odor of ammonia. The precipitate thus formed was collected on a filter-paper, washed with water in five portions of 5 cc. each, and the filtrate with the wash-water preserved. (It will be designated filtrate *C*.) The filter-paper was pierced, and the precipitate washed into a beaker and diluted with water to a volume of about 100 cc., the mixture warmed, and hydrogen sulphide passed through until all the lead was thrown down. The precipitate was collected on a filter and washed with

[1] Methyl alcohol was here used, glucose being more soluble in it than in the ordinary ethyl alcohol. All the alcohol used was first tested carefully to be sure that it contained no reducing substance, by evaporating a portion to dryness on a water-bath, dissolving the residue in water, and testing it by means of Fehling's solution.

[2] Prepared as follows: 192 grams of acetate of lead were dissolved in 640 cc. of distilled water, and 64 grams of yellow oxide of lead added. This was allowed to stand (with frequent shaking), until only a small white precipitate remained. The precipitate was then removed by filtration, and the solution was ready for use, its specific gravity being between 1.23 and 1.24.

five portions of water of 5 cc. each; the filtrate and wash-water collected together, evaporated to dryness, extracted with methyl alcohol, filtered and washed, evaporated to dryness, extracted with water, and the amount of glucose determined as before. (The amount of glucose found in this instance should be the amount present at the end of the process, while amounts found in each of the other instances would be the losses occasioned by the process.) Filtrate *C*, with the wash-water obtained after the addition of ammonium hydroxide, was evaporated to dryness, and after being treated as in the other instances, the glucose present was estimated by Fehling's solution or by the saccharimeter.

Certain difficulties, however, were found in this process which rendered it impracticable. It was found, after evaporating the various solutions to dryness, even though done on a water-bath and with greatest care at a low temperature, that a dark brown, or at times almost black, residue was obtained; which partly dissolved in the alcohol, and rendered the final water solution so dark that it could not be used in the saccharimeter, even in some instances preventing the passage of any light at all through the observation tube. The color of the solution also prevented the use of Fehling's solution, for when it was added to the latter reagent a green solution was obtained, and the exact point of the completion of the reaction could not be determined. On account of the very dark color of the solution it was not possible to dissipate the color sufficiently by dilution without carrying it to such a degree that the small amount of glucose present could not be detected. It was thought that the dark color was probably produced by concentration (during evaporation) of the coloring matters of the urine. It was also thought that the acid found to be present in the solution might produce some reaction on certain of the urinary constituents present and thus cause a dark coloration. Therefore, after the excess of hydrogen sulphide had been driven off by evaporation on a water-bath, a saturated solution of sodium bicarbonate was added, until the solution was rendered neutral, and the evaporation then continued to dryness. It was found, however, that this neutralisation of the acid did not prevent the formation of the dark residue, and hence this method was abandoned.

The method next adopted was to make a number of solutions by dissolving a definite quantity of glucose in a small amount of urine, and then adding more urine until a volume of 100 cc. was obtained. A number of such solutions were made of different

strengths, so that 100 cc. would contain 0.05 gram, 0.1 gram, 0.5 gram, 1.0 gram, or 2.0 grams of glucose. Then the strength of each solution was 0.05 per cent., 0.1 per cent., 0.5 per cent., 1.0 per cent., or 2.0 per cent. Each solution was then carefully divided into two parts of 50 cc. each by means of an accurate pipette. In this way two solutions of exactly equal strength were obtained, which could be readily carried through the process at the same time. (In the following description each solution mentioned is to be understood as having had a volume of 50 cc.) To each portion of urine were added 20 cc. of a 10 per cent. solution of neutral plumbic acetate. The mixture was thoroughly stirred and afterwards filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and washings having been collected together, were poured into a graduated cylinder, the volume of the whole ascertained, and the amount of glucose present determined by taking the average of at least ten observations with the saccharimeter. The saccharimeter tube was carefully washed out, the washings saved and placed with the remainder of the solution, to which were then added 15 cc. of plumbic tribasic acetate, the mixture carefully stirred and filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and washings having been collected together, the volume of the whole solution was ascertained, and the amount of glucose present estimated by the saccharimeter as before. To the whole of this solution, which was carefully saved after the estimation, were added 20 cc. of ammonium hydroxide,[1] and the mixture carefully stirred and filtered. The precipitate was washed with 25 cc. of distilled water in portions of 5 cc. each, and the filtrate and wash-water collected, the volume of the whole ascertained, and the amount of glucose present determined by the saccharimeter.

The precipitate caused by the addition of ammonium hydroxide was suspended in distilled water, and hydrogen sulphide passed through it until all the lead was precipitated, then filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and wash-water were collected together, the volume of the whole solution ascertained, and by the saccharimeter the amount of glucose present was determined.

In three cases a saturated solution of potassium carbonate instead of hydrogen sulphide was used to decompose the lead saccharate.

[1] The solution of ammonium hydroxide employed contained 10 per cent. of NH_3.

In several cases, both neutral plumbic acetate and plumbic tribasic acetate were added before filtration, and the proportion of glucose present then determined, after which the process was carried on as before described.

In a few instances one or more of the determinations were made by Fehling's solution instead of by the saccharimeter.

In some of the solutions the quantity of glucose was not estimated until after the completion of the whole process. Frequently, however, an estimation was also made of the glucose lost in the filtrate after precipitation by ammonium hydroxide.

By these different methods almost all possible conditions of working the original process were obtained, and it was possible to ascertain not only the whole amount of loss caused by the process, but also the steps which involved a loss, and the amount of each.

The saccharimeter used in these experiments was one of the latest Laurent shadow instruments of the largest size.

The 200 mm. tube was frequently used, but when testing a weak solution the 400 mm. tube was used. In every case at least ten observations were made, and the average of these was adopted as showing the amount of glucose present. The glucose was perfectly pure, crystallised and anhydrous, polarising 99.85° to the right as shown by previous experiment.

In two solutions containing 0.05 per cent. of glucose, the average loss caused by the process was found to be 41.00 per cent., the tests being made by Fehling's solution.[1]

A solution containing 0.1 per cent. of glucose showed a loss of 52.60 per cent. by the neutral plumbic acetate and plumbic tribasic acetate, when both were added before the first filtration, and a loss of 66.80 per cent. by the whole process, leaving 14.20 per cent. as the loss caused by the precipitations by ammonium hydroxide and by hydrogen sulphide. However, as only a trace of glucose was found in the filtrate and washings obtained after the precipitation by ammonium hydroxide, this loss must have been caused almost entirely by the precipitation by hydrogen sulphide. In one solution containing the same amount of glucose, only 2.60 per cent. was lost as determined by Fehling's solution in employing the method, and only a trace of glucose was found in the filtrate and washings obtained after precipitation by ammonium hydroxide. In four solutions of the above strength, no glucose was found in the

[1] In the estimations following, the saccharimeter was invariably used, unless Fehling's solution is specially mentioned as having been employed.

filtrate and washings obtained after precipitation by ammonium hydroxide. The average loss in the six solutions employed, containing this amount (0.1 per cent.) of glucose, was 59.16 per cent.

In two solutions, containing 0.5 per cent. glucose, it was found that the average loss in the precipitation by neutral plumbic acetate was 28.22 per cent., while in the precipitation by plumbic tribasic acetate it was 2.76 per cent., making the loss in the two precipitates 30.98 per cent. In the same solutions the average loss by the whole process, as determined by Fehling's solution, was 50.26 per cent., leaving a loss of 19.28 per cent. to be accounted for by the precipitation by ammonium hydroxide and by hydrogen sulphide. But the average loss found in the filtrates obtained after precipitation by ammonium hydroxide was 6.85 per cent., so that the loss caused in the precipitation by hydrogen sulphide was 12.70 per cent. In two solutions, containing the same amount of glucose, both neutral plumbic acetate and plumbic tribasic acetate were added before the first filtration, and the average loss was then found to be 37.82 per cent., and the loss by the whole process was 54.46 per cent., leaving 16.64 per cent. as the loss occasioned by ammonium hydroxide and hydrogen sulphide; but no glucose was found in the filtrates obtained after precipitation by ammonium hydroxide, so that this percentage must represent the loss in the precipitation by hydrogen sulphide. In two solutions, also of this strength, the total loss was found to be 40.20 per cent., both neutral plumbic acetate and plumbic tribasic acetate having been added before filtration. From the six solutions of this strength (0.5 per cent.), the average loss occasioned by the process was 47.33 per cent., while in four of them the loss caused by neutral plumbic acetate and by plumbic tribasic acetate was 34.40 per cent., and the loss to be accounted for by the precipitation by ammonium hydroxide and hydrogen sulphide was 17.96 per cent. But the average loss caused by ammonium hydroxide was 3.29 per cent., leaving 14.67 per cent. as the average loss occasioned by hydrogen sulphide.

In two solutions, containing 1.0 per cent. of glucose, the loss occasioned by neutral plumbic acetate was 8.09 per cent., and that occasioned by plumbic tribasic acetate was 6.85 per cent., making the total loss up to this part of the process 14.94 per cent. After the addition of ammonium hydroxide to these solutions the lead was removed from one of them by a saturated solution of potassium carbonate, and the total loss of glucose was found to be 76.10 per cent., a loss of 62.90 per cent. having been caused by ammo-

nium hydroxide and by the solution of potassium carbonate. No glucose being found in the filtrate from the precipitation by ammonium hydroxide, this average must represent the loss taking place in the precipitation of the lead by potassium carbonate. From the other solution the lead was removed by hydrogen sulphide, and the total loss of glucose was 49.98 per cent., the loss caused by the precipitation by ammonium hydroxide and hydrogen sulphide being 33.30 per cent. But as 8.34 per cent. was found in the filtrate after precipitation by ammonium hydroxide, the remainder (24.98 per cent.) must have been caused by hydrogen sulphide. In a third solution a loss of 30.02 per cent. was caused by the precipitations by ammonium hydroxide and by hydrogen sulphide, and a loss of 40.34 per cent. by the whole process, a loss of 2.02 per cent. by the precipitation by ammonium hydroxide, and this taken from 10.32 per cent., which was the loss occasioned by both ammonium hydroxide and hydrogen sulphide, leaves 8.30 per cent. as the loss caused by the latter. In two solutions, also containing 1.0 per cent. of glucose, the average loss occasioned by the whole process was 64.33 per cent., and the average loss in the five solutions, from which the lead was removed by hydrogen sulphide, was 50.87 per cent.

The loss caused by neutral plumbic acetate in two solutions, containing 2.0 per cent. of glucose, was 8.30 per cent., and that caused by plumbic tribasic acetate was 8.28 per cent., the sum of these losses being 16.58 per cent., while the whole loss was 75.60 per cent., the lead having been precipitated by a saturated solution of potassium carbonate, leaving a loss of 59.02 per cent., which was caused by ammonium hydroxide and by potassium carbonate. By testing the filtrate obtained after precipitation by ammonium hydroxide, a loss was found in one case of 57.82 per cent., and in the other of 20.89 per cent., making an average for the two of 39.35 per cent., which would leave a loss of 19.67 per cent., which must have taken place in the precipitation by potassium carbonate. In two solutions, also containing 2.0 per cent. of glucose, the average total loss was 52.30 per cent., the lead having been precipitated by hydrogen sulphide.

By referring to Table I, it is seen that in one of these solutions (*V*) hardly any loss took place at this part of the process that was not accounted for. If the loss caused by both neutral plumbic acetate and by plumbic tribasic acetate (17.44 per cent.) be subtracted from the total (75.60 per cent.) loss, 58.16 per cent. is left

to be accounted for by ammonium hydroxide and by potassium carbonate. But in the filtrate obtained after precipitation by ammonium hydroxide, 57.82 per cent. of the total amount of glucose was found, leaving only 0.34 per cent. which has not been accounted for. In another solution (*W*) it is observed that although a loss of 59.89 per cent. must have been caused by ammonium hydroxide and by potassium carbonate, yet only 20.89 per cent. was found in the filtrate after precipitation by ammonium hydroxide, and hence there still remains to be accounted for 39.00 per cent. It was thought that some glucose might have been lost in the precipitate caused by the addition of a solution of potassium carbonate, and hence in each case this precipitate was diffused in water, and hydrogen sulphide passed through it until all the lead was precipitated. The precipitate of lead sulphide was collected by filtration, and washed with 25 cc. of water in five portions of 5 cc. each. The filtrate and washings were tested, but no glucose was found. However, before passing hydrogen sulphide through the precipitate of lead carbonate diffused in water, the mixture was warmed on a water-bath, and it was then noticed that a dark coloration appeared. No doubt this was caused by the action of an excess of alkali on the glucose present, causing the formation of melassic acid, etc.

By examination of the tables it will be seen that the process does not give satisfactory results if the lead is precipitated by a saturated solution of potassium carbonate, for in the three solutions in which it was tried the average loss was 75.77 per cent. The average loss discovered in the filtrates obtained after precipitation by ammonium hydroxide was 26.23 per cent., leaving 49.54 per cent. as the percentage probably lost in the precipitation caused by the solution of potassium carbonate.

It is evident, then, that less than 25.00 per cent. of the glucose, originally present in the urine, can be expected to be found after employing the process in this way.

It is also evident that in all of the processes employed there is a steady loss taking place throughout. By referring to Table III it is observed that after precipitation by neutral plumbic acetate, in two solutions, containing each 0.25 gram of glucose, only 71.78 per cent. was recovered; and in two solutions containing 0.5 gram of glucose only 91.91 per cent., and in two solutions containing 1.0 gram of glucose, 91.70 per cent. was recovered, giving an average of 85.13 per cent. recovered in the six solutions tested.

After precipitation by plumbic tribasic acetate in one solution, containing 0.05 gram of glucose, 47.40 per cent. was recovered. In four solutions, each containing 0.25 gram, 65.60 per cent. was recovered. In three solutions, each containing 0.5 gram, 80.04 per cent. was recovered, and in two solutions, each containing 1.0 gram, 83.42 per cent. was recovered. In these ten solutions, then, the average amount recovered was 71.67 per cent.

At the end of the process in two solutions, each containing 0.025 gram of glucose, 59.00 per cent. was recovered. In six solutions, each of which contained 0.05 gram of glucose, 40.84 per cent. was recovered. In six solutions, each of which contained 0.25 gram, 51.69 per cent. was recovered. In five solutions, each of which contained 0.5 gram of glucose, 49.13 per cent., and in two solutions, each containing 1.0 gram of glucose, 47.70 per cent. was recovered.

When hydrogen sulphide is used to precipitate the lead, it is certain that no one step in the process can be said to be specially faulty. The loss occasioned by the precipitation by neutral plumbic acetate (as seen by Table V) is greater than that caused by plumbic tribasic acetate, but neither of these losses is equal to that which takes place at later steps in the process.

Moreover, the losses are not uniform, but very variable in different solutions. And in the experiments this variation was found to exist, even though the solutions were subjected to exactly the same conditions, and even when the corresponding precipitates, in each case, were washed the same number of times and with equal volumes of water. Hence, from any amount of glucose found after employing the process, it could not be determined how much had originally been present in the urine.

The process certainly removes the interfering substances from the urine; but even for qualitative work, if no reaction for glucose could be obtained after making use of the process, it would be by no means certain that no glucose had been originally present in the urine.

In completing this paper the writer desires to express his great indebtedness to Dr. John Marshall, Demonstrator of Chemistry in the Medical Department of the University of Pennsylvania, for his valuable suggestions in carrying on the work, and to whom any success attained in the experiments is largely due.

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TABLE I.—*Showing Loss after Each Step of the Process and Per Cent. of that Loss.*

	Cc. of Solution Employed.	Amount of Glucose Present.	Loss after Plumbic Acetate.	Per Cent. of Previous Loss.	Loss Caused by Tribasic Acetate.	Per Cent. of Loss.	Sum of Previous Losses.	Per Cent. of Losses.	Total Loss.	Per Cent. of Total Loss.	Amount Finally Present.	Amount Finally Present when K_2CO_3 was used.	Loss in NH_4HO Filtrate.	Per Cent. of Loss.	Loss caused by NH_4HO, H_2S or K_2CO_3 (Estimated).	Per Cent. of Loss.
A	50	0.025	.....	.....	.....	.....	.....	.....	0.0097	38.80	0.0153[1]	.....	.....	.....	.....	.....
B	50	0.025	.....	.....	.....	.....	.....	.....	0.0168	43.20	0.0142[1]	.....	.....	.....	.....	.....
C	50	0.05	.....	.....	.....	.....	.....	.....	0.0305	61.00	0.0195	.....	0	.....	.....	.....
D	50	0.05	.....	.....	.....	.....	.....	.....	0.0419	83.80	0.0081	.....	0	.....	.....	.....
E	50	0.05	.....	.....	.....	.....	.....	.....	0.0013	2.60	0.0487[1]	.....	Trace.	.....	0.0071	14.20
F	50	0.05	.....	.....	.....	.....	0.0263	52.60	0.0334	66.80	0.0166	.....	Trace.	.....	.....	.....
G	50	0.05	.....	.....	.....	.....	.....	.....	0.0354	70.80	0.0146	.....	0	.....	.....	.....
H	50	0.25	.....	.....	0.0039	1.56	0.0847	33.88	0.0350	70.00	0.0150	.....	.....	.....	0.0416	16.64
I	50	0.25	32.32	32.32	0.0099	3.96	0.0702	28.08	0.1263	50.52	0.1237[1]	.....	0.0141	5.64	.....	.....
J	50	0.25	24.12	.....	.....	.....	0.0944	37.76	0.1250	50.00	0.1250[1]	.....	0.0188	7.52	0.0548	21.92
K	50	0.25	.....	.....	.....	.....	0.0947	37.88	0.1110	44.40	0.1390	.....	0	.....	0.0160	6.64
L	50	0.25	.....	.....	.....	.....	.....	.....	0.1613	64.52	0.0887	.....	0	.....	0.0666	26.64
M	50	0.25	.....	.....	.....	.....	.....	.....	0.1126	45.04	0.1374	.....	.....	.....	.....	.....
N	50	0.25	.....	.....	.....	.....	.....	.....	0.0884	35.36	0.1616	.....	.....	.....	.....	.....
O	50	0.5	7.02	0.0309	6.18	0.0660	13.20	0.3865	76.10	.....	0.1195	.....	0	.....	0.3145	62.90
P	50	0.5	0.0458	9.16	0.0376	7.52	0.0834	16.68	0.2499	49.98	0.2501	.....	0.0417	8.34	0.1665	33.32
R	50	0.5	.....	.....	.....	.....	0.1501	30.02	0.2017	40.34	0.2983	.....	0.0101	2.02	0.0516	10.32
S	50	0.5	.....	.....	.....	.....	.....	.....	0.1718	34.36	0.3282	.....	.....	.....	.....	.....
T	50	0.5	.....	.....	.....	.....	.....	.....	0.2856	57.12	0.2144	.....	.....	.....	.....	.....
U	50	0.5	.....	.....	.....	.....	.....	.....	0.3627	72.54	0.1373	.....	.....	.....	.....	.....
V	50	1.0	0.1157	11.57	0.0587	5.87	0.1744	17.44	0.7560	75.60	.....	0.2440	.....	.....	.....	.....
W	50	1.0	0.0594	5.04	0.1068	10.68	0.1572	15.72	0.7561	75.61	.....	0.2439	0.5782	57.82	0.5816	58.16
X	50	1.0	.....	.....	.....	.....	.....	.....	0.4919	49.19	0.5081	.....	0.2089	20.89	0.5989	59.89
Y	50	1.0	.....	.....	.....	.....	.....	.....	0.5560	55.60	0.4440	.....	.....	.....	.....	.....

[1] These estimations were made by means of Fehling's solution.

TABLE II.—*Averages of the Amounts of Glucose Recovered and Lost at Different Stages of the Process.*

Number of Solutions represented in Averages.	Corresponding Solutions in Table I.	Amount of Glucose in each Solution.	Amount Present after use of Lead Acetate.	Loss.	Amount Present after use of Tribasic Acetate.	Averages of Amounts Present.	Loss.	Averages of Loss.	Amount Finally Present.	Averages of Amounts Finally Present.	Final Losses.	Averages of Final Losses.	Number of Solutions represented in Previous Averages.
2	A, B	0.025	.....	.....	.....	.....	.....	.....	0.0147	0.0147	0.0103	0.0103	2
1	F	0.05	.....	.....	0.0237	0.0237	0.0263	0.0263	0.0166	0.0204	0.0334	0.0296	6
5	C, D, E, G, H	0.05	.....	.....	.....	.....	.....	.....	0.0212		0.0288		
2	I, J	0.25	0.1794	0.0706	0.1725	0.1639	0.0775	0.0861	0.1243	0.1292	0.1257	0.1208	6
2	K, L	0.25	.....	.....	0.1554		0.0946		0.1138		0.1362		
2	M, N	0.25	.....	.....	.....	.....	.....	.....	0.1495		0.1005		
2	O, P	0.5	0.4595	0.0405	0.4253	0.4001	0.0747	0.0999	[1]0.2501		0.2499	0.2544	5
1	R	0.5	.....	.....	0.3499		0.1501		0.2983	0.2456	0.2017		
3	S, T, U	0.5	.....	.....	.....	.....	.....	.....	0.2266		0.2734		
2	V, W	1.0	0.9170	0.0830	0.8342	0.8342	0.1658	0.1658	[2]0.2440	.....	0.7560	0.5240	2
2	X, Y	1.0	.....	.....	.....	.....	.....	.....	0.4760	0.4760	0.5240		

[1] 0.2501 is the amount recovered in *one* of the solutions. The other solution was not considered, as in it the lead was precipitated by K_2CO_3 instead of by H_2S.
[2] 0.2440 was not used in making up the average, as in these solutions the lead was precipitated by K_2CO_3.

TABLE III.—*Averages of the Percentages Recovered and Lost at Different Stages of the Process.*

Number of Solutions represented in the Averages.	Corresponding Solutions in Table I.	Amount of Glucose in each Solution.	Per Cent. Present after use of Lead Acetate.	Per Cent. of Loss.	Per Cent. Present after use of Tribasic Acetate.	Averages of percentages Present.	Per cent. of Losses.	Average of percentages Lost.	Percentage Finally Present.	Average percentage Finally Present.	Per Cent. of Total Losses.	Average Per Cent. of Total Losses.	Number of Solutions represented in Previous Averages.
2	A, B	0.025	.....	.....	.....	.....	.....	.....	59.00	59.00	41.00	41.00	2
1	F	0.05	.....	.....	47.40	47.40	52.60	52.60	33.20	40.84	66.80	59.16	6
5	C, D, E, G, H	0.05	.....	.....	.....	.....	.....	.....	42.36		57.64		
2	I, J	0.25	71.78	28.22	69.02	65.60	30.98	34.40	49.74	51.69	50.26	48.31	6
2	K, L	0.25	.....	.....	62.18		37.82		45.54		54.46		
2	M, N	0.25	.....	.....	.....	.....	.....	.....	59.80		40.20		
2	O, P	0.5	91.91	8.09	85.06	80.04	14.94	19.96	[1]50.02	49.13	[1]49.98	50.87	5
1	R	0.5	.....	.....	69.98		30.02		59.66		40.34		
3	S, T, U	0.5	.....	.....	.....	.....	.....	.....	45.32		54.67		
2	V, W	1.0	91.70	8.30	83.42	83.42	16.58	16.58	[2]24.40	.....	75.60	52.40	2
2	X, Y	1.0	.....	.....	.....	.....	.....	.....	47.60	47.60	52.40		

[1] 50.02 is the percentage recovered in one of the solutions. The other solution was not considered, as in it the lead was precipitated by K_2CO_3 instead of by H_2S.
[2] In these solutions the lead was precipitated by K_2CO_3 and 24.40 per cent. was not considered in making up the average.

TABLE IV.—*Amount of Glucose Present in Each Solution after Each Step in the Process.*

	Volume of each Solution.	Amount of Glucose in each.	Amount Present after use of Lead Acetate.	Amount Present after the use of Tribasic Acetate.	Final Amount Present.	Final Amount Present when K_2CO_3 was used.
A	50 cc.	0.025	.....	.....	0.0153 (F)	.....
B	50 cc.	0.025	.....	.....	0.0142 (F)	.....
C	50 cc.	0.05	.....	.....	0.0195	.....
D	50 cc.	0.05	.....	.....	0.0081	.....
E	50 cc.	0.05	.....	.....	0.0487 (F)	.....
F	50 cc.	0.05	.....	0.0237	0.0166	.....
G	50 cc.	0.05	.....	.....	0.0146	.....
H	50 cc.	0.05	.....	.....	0.0150	.....
I	50 cc.	0.25	0.1692	0.1653	0.1237 (F)	.....
J	50 cc.	0.25	0.1897	0.1798	0.1250 (F)	.....
K	50 cc.	0.25	.....	0.1556	0.1390	.....
L	50 cc.	0.25	.....	0.1553	0.0887	.....
M	50 cc.	0.25	.....	.....	0.1374	.....
N	50 cc.	0.25	.....	.....	0.1616	.....
O	50 cc.	0.5	0.4649	0.4340	.....	0.1195
P	50 cc.	0.5	0.4542	0.4166	0.2501	.....
R	50 cc.	0.5	.....	0.3499	0.2983	.....
S	50 cc.	0.5	.....	.....	0.3282	.....
T	50 cc.	0.5	.....	.....	0.2144	.....
U	50 cc.	0.5	.....	.....	0.1373	.....
V	50 cc.	1.0	0.8843	0.8256	.....	0.2440
W	50 cc.	1.0	0.9496	0.8428	.....	0.2439
X	50 cc.	1.0	.....	.....	0.5081	.....
Y	50 cc.	1.0	.....	.....	0.4440	.....

(F) These results were obtained by the use of Fehling's solution.

TABLE V.—*Average Percentages of Losses Caused at Different Stages of the Process.*

No. of Solutions.	Percentage of each.	Amount of Glucose in each.	Average Loss after use of Lead Acetate.	Average Loss caused by use of Tribasic Acetate.	Sum of these Losses.
2	0.5	0.25	28.22	2.76	30.98
2	1.0	0.5	8.09	6.85	14.94
2	2.0	1.0	8.30	8.28	16.58
Average of above losses.....			14.87	5.96	20.83

TABLE VI.—*Average Percentages of Losses at Different Stages of the Process in all of the Solutions.*

No. of Solutions.	Amount of Glucose Present after use of Lead Acetate.	Loss after Lead Acetate.	Per Cent. of Loss by Tribasic Acetate.	Per Cent. of Amount Present after Tribasic Acetate.	Sum of Previous Losses.	Per Cent. of Total Loss.	Per Cent. Finally Present.
6	85.13	14.87	5.96	79.17	20.83	.....	.....
4	.....	.....	.....	60.44	39.56	.....	.....
	Average of above percentages			71.67	28.33	52.36[1]	47.64
14						50.52	49.48
	Average of above percentages[2].....					51.71	48.29

TABLE VII.—*Average Amounts of Glucose Recovered after the Process, with Percentages.*

No. of Solutions.	Per Cent. of Glucose in each Solution.	Amount of Glucose in Grams in each Solution.	Amount of Glucose Recovered.	Per Cent. of Glucose Recovered.
2	0.05	0.025	0.0147	59.00
6	0.1	0.05	0.0204	40.84
6	0.5	0.25	0.1292	51.69
5	1.0	0.5	0.2456	49.13
2	2.0	1.0	0.4760	47.60

[1] Only seven of the solutions were considered in making this average, as in the remaining three of the ten solutions the lead was precipitated by K_2CO_3 instead of by H_2S.

[2] Viz.: in all of the twenty-one solutions employed, in which the lead was precipitated by hydrogen sulphide.

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